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made, for all measurements will be vitiated by the adsorption effect observed in this research.

The replacement of the law by a more correct equation of state, *e.g.*, $p(v - b) = nRT$, would not materially affect the conclusions set forth. The equation on which the adsorption calculations are based is $n - n_1 = (p/T - p_1/T_1)v/R$ (see McHaffie and Lenher, *loc. cit.*, p. 1565); using the other equation of state, this becomes $n - n_1 = (p/T - p_1/T_1)(v - b)/R$, where $b$ is the volume occupied by the benzene molecules themselves. For the adsorption vessels used, $v$ varies from 5·317 c.c. to 13·307 c.c.; in the experiments, the values of $b$ vary from $1{\cdot}3 \times 10^{-5}$ to $2{\cdot}7 \times 10^{-5}$ c.c. Thus it is clear that the ratio $v/(v - b)$ may be taken to be equal to unity for the present purpose, and it is obvious that the application of a correction to the Boyle–Charles law is unnecessary in the present case of a vapour near saturation at ordinary temperatures.

*Summary.*

The adsorption of benzene vapour at pressures above 90% of the saturated equilibrium pressure has been measured on the surfaces of glass, fused quartz, and platinum. An unusually great adsorption on the platinum surface was observed. The free energy changes accompanying the adsorption were calculated.

The isosteric heat of adsorption at constant pressure of benzene vapour on platinum has been calculated from the adsorption isotherms; within the accuracy of calculation, it is found to be of the same magnitude as the latent heat of condensation to liquid.

The adsorption of vapours on solid surfaces over a wide range of pressure is briefly discussed.

A table is given showing the thickness of films exerting the saturated equilibrium pressure.

The author expresses his thanks to Professor F. G. Donnan, F.R.S., for his constant interest and valuable advice during the progress of this research.

THE SIR WILLIAM RAMSAY LABORATORY OF PHYSICAL AND INORGANIC CHEMISTRY, UNIVERSITY COLLEGE, LONDON. [*Received, November 9th*, 1926.]

# XLV.—*The Density of Boron Trichloride and the Suspected Variation in the Atomic Weight of Boron.*

By Henry Vincent Aird Briscoe, Percy Lucock Robinson, and Harold Cecil Smith.

A technique for the determination and comparison of liquid densities with great precision by means of glass floats has recently been developed in this laboratory (Robinson and Smith, J., 1926, 1262) and applied to the problem of the constancy of the atomic weight of silicon derived from different sources. As the differences disclosed in this case did not exceed 0·005 unit, *i.e.*, 1 part in 5612, it seemed advisable to apply this method to boron, where a maximum difference of 0·023 unit, *i.e.*, 1 part in 540, was originally found by measuring the ratio $BCl_3 : 3Ag$ (Briscoe and Robinson, J., 1925, **127**, 696) and subsequently confirmed by a measurement of the density of pure fused boric oxide glass prepared from the same sources (Briscoe, Robinson, and Stephenson, J., 1926, 70).

### *Outline of the Present Investigation.*

In the last stage of the purification, the samples of boron trichloride (Briscoe and Robinson, *loc. cit.*) had been divided by fractional vacuum-distillation into three fractions, and the middle fraction had been used for analysis. In the present investigation, the remaining fractions of each sample were combined and purified by two further distillations in a vacuum, with the rejection of lighter and heavier fractions in each distillation, and the densities of the final main fractions were determined. In the case of two out of the three samples, the liquids forming the final main fractions were distilled fractionally on to and away from the floats, and the densities of the several runnings were thus obtained. From these data, the mean density of boron trichloride, its coefficient of thermal expansion, and the relative atomic weight of the samples of boron present in the various fractions were calculated.

### *Preparation of Boron Trichloride.*

The original sources of the boron used in the three preparations of the trichloride were :

No. 1. Colemanite (calcined) from Death Valley, California, U.S.A.

No. 2. Crude boric acid from the neighbourhood of Volterra, Tuscany.

No. 3. Boracite from Sultan Tchair, Asia Minor.

Each sample, after receiving the uniform and rigorous purification

previously described, had been finally divided into five fractions designated $T_6$, $M$III, $M$II, $M$I, and $H_5$ (J., 1925, **127**, 704, Fig. 1). $T_6$ and $H_5$ were small tail- and head-fractions of about 5—10 c.c., $M$II was the main fraction for analysis, and $M$III and $M$I were tail- and head-fractions similar in size to $M$II. $M$III and $M$I had been preserved in the original containers, having special joints which were now attached to a train (Fig. 1) carrying a head-fraction bulb, H, and a container with a special joint, A. $M$III and $M$I were arranged so that the plunger tubes, P, were at right angles to one another, thus enabling the capillary of either special joint to be

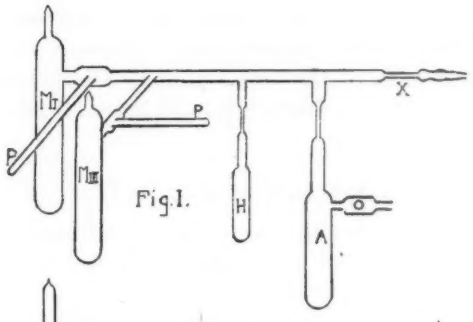

Fig. 1.

Fig. 3.

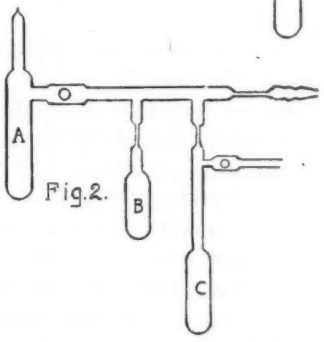

Fig. 2.

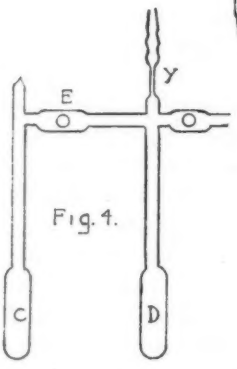

Fig. 4.

broken by moving the apparatus in the appropriate way. The apparatus was internally cleaned with the usual elaborate precautions, and after assembly was evacuated at X six times, being heated to 150° during each evacuation and thereafter slowly refilled with carefully dried air. Then it was sealed off with the McLeod gauge registering a pressure of 0·01 mm. The special joint of $M$I was then broken and a head-fraction was distilled into H and sealed off. The rest of the contents of $M$I was distilled into A. The special joint of $M$III was then broken and its contents were distilled into A with the exception of a small tail-fraction; A was then removed by sealing off. This procedure was based on the assumption that, whatever impurity the material might contain, that in $M$I would

probably have a lower b. p. and that in $M_{III}$ a higher b. p. than boron trichloride.

The vessel A was now attached to a second train (Fig. 2) which, after cleaning and drying as described above, was sealed off from the pump when the pressure had remained below 0·01 mm. for 30 minutes. B was thoroughly cooled with liquid air, the special joint of A was broken, and the small head-fraction which immediately collected in B was sealed off. C, which contained the two floats, was then cooled with liquid air and the material in A was very slowly and completely distilled at a temperature well below 0°. There were barely visible solid residues left in A from samples No. 2 (Tuscany) and No. 3 (Asia Minor), but there was a small although perceptibly greater residue in No. 1 (California). After the removal of C this residue, which was of the usual gummy character, was warmed and intumesced in the manner previously noted (Briscoe and Robinson, *loc. cit.*).

*The Preparation and Standardisation of the Floats.*

(The experimental work following is given in outline, and the references, unless otherwise stated, are to Robinson and Smith, J., 1926, 1262, where details may be found.)

The "Durosil" glass floats were prepared precisely as were those used in the determination of the density of silicon tetrachloride; they were rather shorter, as the volumes of the liquids available were less, and the densities of the individual floats of each series were closer together, the maximum difference being in the upper series 0·000194, and in the lower 0·000181.

Previous workers have given for the density of boron trichloride 1·35 at 17·5° (Wohler and Deville, *Compt. rend.*, 1857, **45**, 888) and 1·43386 at 0°/4° (Ghira, *Z. physikal. Chem.*, 1894, **12**, 768; *Gazzetta*, 1893, **23**, i, 452). As these results were too divergent for the present purpose, a preliminary measurement was made. An all-glass hydrometer (Fig. 3) (suitably constructed from a piece of glass tubing of 0·8 cm. bore, with a solid sinker, a body 2 cm. long, and a fine stem 6 cm. long and 0·6 mm. in diameter) was calibrated in a series of bromotoluene–ethyl alcohol mixtures by measuring the length of exposed stem with a cathetometer. The densities of these mixtures were obtained with a Westphal balance. This little hydrometer, which had a range of 1·360—1·417 for a stem exposure of 2·390 cm. and gave readings to about 0·001, is detailed here because of its obvious convenience for such purposes as the present. A number of fractions of boron trichloride from the four-column still (Briscoe and Robinson, *loc. cit.*) were collected into a single vessel, sealed up over mercury for a fortnight, and then distilled in a

vacuum on to the hydrometer. A density of 1·350/11° was indicated, which is in reasonable agreement with the value of Wohler and Deville.

An extensive series of liquids and mixtures was reviewed with regard to suitability for float calibration, *n*-propyl bromide (*d* 1·364/18°) being eventually selected. This liquid, from The British Drug Houses, Ltd., had *d* 1·346/19°, as measured by the Westphal balance. Two floats, with flotation-temperatures 10·14° and 15·20°, respectively, in *n*-propyl bromide, were tried out in the boron trichloride previously used for the hydrometer test by transferring the liquid *via* a special joint to another vessel containing the floats. The flotation-temperatures in boron trichloride were 7·45° and 11·19°, respectively; and it was therefore decided to work to flotation-temperatures of 10° and 12°, respectively (*i.e.*, below the b. p. at atmospheric pressure), these being equivalent, respectively, to 14° and 16° in *n*-propyl bromide. It was early noticed that the density of this liquid decreased with time (compare bromobenzene, *loc. cit.*), and the specimen used in the final calibration was therefore purified by one rough, followed by two careful, distillations with the rejection of head- and tail-fractions, the boiling points, taken every minute, having mean values 71·40°/756·8 mm. and 71·75°/760·2 mm. The standardisation of the floats was repeated with the once-, twice-, and thrice-distilled *n*-propyl bromide in the same apparatus (except that the float-lifter was of platinum, as nichrome was attacked), and with all the precautions previously described (*loc. cit.*), 161 flotation-temperatures being taken. As even the purified liquid tended to decrease in density with time, the final measurements for the six floats were completed within 8·5 hours of the third distillation, the flotation-vessel being then corked up. On the following day, the density of the liquid was determined at 16·857° and 20·873°, with the pyknometers and by the method previously described (*loc. cit.*), the results being 1·351288 and 1·344572, respectively. Immediately afterwards two check flotation-temperatures were taken, the same liquid being used to establish the constancy of its density. These results are given in Table I which illustrates both the change in density of the *n*-propyl bromide and the increased permanency of its density with purification.

*The Density of the Three Samples of Boron Trichloride at* 11°.

Flotation-temperatures were obtained in exactly the manner described for silicon tetrachloride, except that, as the temperatures were constantly below that of the room, the bath was maintained in the required condition by a variable stream of ice-cold water from another tank. This arrangement was found to give excellent

TABLE I.

The Standardisation of the Floats in *n*-Propyl Bromide.

| Float. | Flot.-temp. ($C_3H_7Br$ once distilled). | Flot.-temp. ($C_3H_7Br$ twice distilled). | Flot.-temp. ($C_3H_7Br$ thrice distilled). | Density (g./c.c.). | Flot.-temp. (check after density detern.). |
|---|---|---|---|---|---|
| U | 13·884° | 16·922° | 17·229° | 1·350666 | 17·223° |
| Y | 13·794 | 16·838 | 17·134 | 1·350825 | |
| Z | 13·819 | 16·819 | 17·121 | 1·350847 | |
| V | 15·809 | 18·909 | 19·223 | 1·347331 | |
| W | 15·839 | 18·787 | 19·106 | 1·347525 | |
| X | 15·849 | 18·802 | 19·123 | 1·347499 | 19·111 |

temperature regulation. About 130 flotation-temperatures were observed and those actually used differed by less than 0·010° for rising and falling temperatures. The floats showed markedly less tendency to become electrically charged than was the case in silicon tetrachloride (*loc. cit.*); the charges were most in evidence in the Asiatic sample, but even these were sufficiently reduced after two hours to allow flotation-temperatures to be taken. The charges were again positive in character (*loc. cit.*). Table II gives these results with the corresponding densities, the value $15 \times 10^{-6}$ being used as the coefficient of cubical expansion of "Durosil" glass (Robinson and Smith, J., 1926, 3152). Table III gives the coefficients of cubical expansion calculated from the same data, together with the calculated probable error of the mean.

TABLE II.

The Density of Boron Trichloride.

| Source. | Float. | F.-t. in $BCl_3$. | $D$ at f.-t. | $D$ of $BCl_3$ at 11·000°. | Diff. from mean. |
|---|---|---|---|---|---|
| California | Y | 10·351° | 1·350963 | 1·349478 | +0·000157 |
| | X | 11·800 | 1·347647 | | |
| Tuscany | U | 10·326 | 1·350805 | 1·349273 | −0·000048 |
| | V | 11·788 | 1·347482 | | |
| Asia Minor | Z | 10·229 | 1·350987 | 1·349213 | −0·000108 |
| | W | 11·666 | 1·347676 | | |
| | | | Mean | 1·349321 | ±0·000104 |

TABLE III.

The Coefficient of Thermal Expansion of Boron Trichloride.

| Source. | Coeff. of exp. | Diff. from mean. |
|---|---|---|
| California | 0·0016981 | +0·0000004 |
| Tuscany | 0·0016868 | −0·0000109 |
| Asia Minor | 0·0017073 | +0·0000096 |
| Mean | 0·0016977 | ±0·0000070 |

Calculated probable error on mean, 0·0000040.

In Table IV are given the relative atomic weights of the boron present in the three samples, calculated by making the usual assump-

tions (*loc. cit.*) and taking Asiatic boron trichloride, $d$ 1·349213 and atomic weight 10·818, as standard (the same standard is used throughout this paper). Table IV also includes for the sake of comparison the previous results of Briscoe and Robinson (*loc. cit.*) and of Briscoe, Robinson, and Stephenson (*loc. cit.*).

TABLE IV.

| Source. | $D$. | At. wt. from $D$. | At. wt. from $BCl_3 : 3Ag$. | At. wt. from $D$ of $B_2O_3$. |
|---|---|---|---|---|
| California ..... | 1·349478 | 10·841 | 10·841 | 10·847 |
| Tuscany ..... | 1·349273 | 10·823 | 10·823 | 10·825 |
| Asia Minor ..... | 1·349213 | 10·818 | 10·818 | 10·818 |

For reasons dealt with more particularly below, the Californian and the Asiatic material underwent the further investigation next described. The flotation-vessels were severally attached to second containers constructed with long stems and special joints as illustrated (Fig. 4), to enable both vessels to be submerged to the same level in the bath. These were cleaned and dried with the usual precautions, being evacuated and refilled with dry air six times, with heating each time to about 150°, and were finally sealed off at Y when a pressure of 0·007 mm. had been registered for 30 minutes. After final check flotation-temperatures had been taken, the liquid in C was cooled with solid carbon dioxide and the special joint, E, was broken. This arrangement enabled the following operations to be performed: (*a*) distillation from C to D with determination of densities at intervals so long as there remained sufficient liquid to allow of the movement of one float; (*b*) pouring from C to D and distillation from D to C with density determinations at intervals as soon as there was sufficient liquid in C; (*c*) washing, by distilling a little liquid from the main bulk into the other vessel and then pouring back. Actually the material in C was distilled into D in stages, solid carbon dioxide being used as the cooling agent and bumping avoided by slightly cooling C; densities were taken at intervals. The residual liquid was then poured into D, and on three occasions small quantities were distilled into C and poured back into D. From D, which now held the whole of the liquid, it was distilled in stages on to the clean floats in C, densities being taken at intervals as soon as possible. These two sets of measurements were then repeated as a check. The numerous observations of flotation-temperatures in which two floats were used soon demonstrated that the temperature interval between the two floats was sufficiently constant to permit the use of one float only when this was convenient. Tables V and VI give the data for the Californian and the Asiatic boron trichloride, respectively.

## Table V.

### Californian Boron Trichloride.

1. Distilling from C to D.

| Amount on floats. | Flotation-temperatures. Float Y. | Float X. | Observed temp.-interval. | Density. |
|---|---|---|---|---|
| Total. | 10·351° | 11·800° | 1·449° | 1·349478 |
| 11/12 tail. | 10·366 | 11·816 | 1·450 | 1·349514 |
| 10/12 ,, | 10·381 | 11·829 | 1·448 | 1·349545 |
| 9/12 ,, | 10·392 | 11·844 | 1·452 | 1·349575 |
| 8/12 ,, | 10·406 | 11·854 | 1·448 | 1·349602 |
| 7/12 ,, | | 11·871 | | 1·349639 |
| | | | Mean 1·449 | |

2. Distilling from D to C.

| | | | | |
|---|---|---|---|---|
| 6/12 head. | | 11·738 | | 1·349337 |
| 7/12 ,, | | 11·738 | | 1·349337 |
| 8/12 ,, | | 11·741 | | 1·349344 |
| 9/12 ,, | | 11·741 | | 1·349344 |
| 10/12 ,, | | 11·744 | | 1·349351 |
| 11/12 ,, | | 11·756 | | 1·349378 |
| Total (distilled). | | 11·796 | | 1·349469 |
| Total (washed).* | 10·350 | 11·800 | 1·450 | 1·349478 |

## Table VI.

### Asiatic Boron Trichloride.

1. Distilling from C to D.

| Amount on floats. | Flotation-temperatures. Float Z. | Float W. | Observed temp.-interval. | Density. |
|---|---|---|---|---|
| Total. | | 11·670° | | 1·349212 |
| 13/15 tail. | | 11·683 | | 1·349241 |
| 11/15 ,, | | 11·688 | | 1·349252 |
| 9/15 ,, | | 11·699 | | 1·349279 |
| 7/15 ,, | 10·256° | 11·701 | 1·445° | 1·349281 |
| 5/15 ,, | 10·259 | 11·707 | 1·448 | 1·349293 |

2. Distilling from D to C.

| | | | | |
|---|---|---|---|---|
| 7/17 head. | 10·226 | 11·666 | 1·440 | 1·349213 |
| 10/17 ,, | | 11·673 | | 1·349219 |
| 12/17 ,, | 10·222 | 11·662 | 1·440 | 1·349207 |
| 14/17 ,, | | 11·670 | | 1·349212 |
| 16/17 ,, | 10·223 | 11·668 | 1·445 | 1·349213 |
| Total (distilled). | | 11·679 | | 1·349234 |
| Total (washed).* | | 11·680 | | 1·349235 |
| | | | Mean 1·444 | |

* "Washed" indicates that a small amount of liquid had been poured back on to the residue and then poured forward again, and this operation repeated three times.

### *Discussion of Results.*

*The Density.*—The relative error of the densities given above is probably less than $\pm$ 0·000002, whilst the absolute value may, for reasons given elsewhere (*loc. cit.*), be as much as $\pm$ 0·00005 from the truth. The authors conclude that the values for the Californian,

Tuscan, and Asiatic materials are 1·349353, 1·349273, and 1·349211, respectively, giving a mean density of 1·349279 at 11·000° ± 0·005° for an average sample of boron trichloride, these results being absolute and independent of the expansion of glass.

*The Coefficients of Expansion.*—The values given in Table VII for Californian and Asiatic materials are both derived from the mean of six intervals of temperature, whilst that for Tuscany boron is taken from Table III. The coefficients of expansion at 10° have a mean value of 0·0016954 with an error probably less than ±0·000005, and a calculated probable error of ± 0·0000030. These results are absolute. Apparently this physical constant for boron trichloride has not been determined previously.

TABLE VII.

| Source. | Mean temp.-interval. | Coeff. of exp. | Diff. from mean. |
|---|---|---|---|
| California ..... | 1·449 | 0·0016981 | +0·0000027 |
| Tuscany ..... | 1·462 | 0·0016868 | −0·0000086 |
| Asia Minor ..... | 1·444 | 0·0017014 | +0·0000060 |
| | Mean | 0·0016954 | ±0·0000058 |

Calculated probable error, 0·0000030.

*The Relative Atomic Weights.*—The relative atomic weights derived from a comparison of the density of the whole bulk of material from the three sources (see Table III) are in remarkable agreement with those of Briscoe and Robinson (*loc. cit.*), but as they were combinations of a head- and a tail-fraction taken before and after the portion analysed, with comparatively little subsequent rejection, it was clearly desirable to ascertain whether they were of uniform composition. Previous work upon the $BCl_3 : 3Ag$ ratio had indicated that a higher apparent atomic weight was to be expected in both the head- and the tail-fractions. The higher value for the latter was easily explained by assuming the presence of boric oxide or silicon tetrachloride, whereas the higher value for the head fraction, although it had been independently observed by Baxter and Scott (*Proc. Amer. Acad. Arts Sci.*, 1923, **59**, 21), was difficult to account for, because the impurities to be anticipated here, *e.g.*, hydrogen chloride and chlorine, are such as would give a lower apparent atomic weight. From the data in Tables V and VI the density and corresponding apparent atomic weight of the separate fractions have been calculated and are given in Table VIII.

It is evident that in each case the extreme heads show a markedly lower density, and it may be presumed that this is related to the unexplained higher apparent atomic weight in the fractions mentioned above. On the other hand, the higher density in the case of the tail-fractions is very obvious, particularly in those of the Californian sample, where, as its effect is somewhat spread, *i.e.*, over the

TABLE VIII.

| Source : California. | | | Source : Asia Minor. | | |
|---|---|---|---|---|---|
| Head-fractn. Twelfth. | Density. | At. wt. | Head-fractn. Two-fifteenths. | Density. | At. wt. |
| 1st | 1·349082 | 10·807 | 1st | 1·349024 | 10·802 |
| 2nd | 1·349204 | 10·817 | 2nd | 1·349181 | 10·815 |
| 3rd | 1·349285 | 10·824 | 3rd | 1·349131 | 10·811 |
| 4th | 1·349359 | 10·831 | 4th | 1·349272 | 10·823 |
| 5th | 1·349343 | 10·829 | 5th | 1·349251 | 10·821 |
| 6th | | | Seventeenth. | | |
| 7th | 1·349337 | 10·829 | 8th, 9th, and 10th | 1·349233 | 10·819 |
| 8th | 1·349393 | 10·833 | 11th and 12th | 1·349147 | 10·812 |
| 9th | 1·349344 | 10·829 | 13th and 14th | 1·349242 | 10·820 |
| 10th | 1·349414 | 10·836 | 15th and 16th | 1·349220 | 10·818 |
| 11th | 1·349648 | 10·856 | 17th | 1·349570 | 10·849 |
| 12th | 1·350470 | 10·927 | | | |

10th, 11th, and 12th twelfths, it may be due to the presence of silicon tetrachloride as well as boric oxide. With the Asiatic material the effect is only noticeable in the last seventeenth and is probably accounted for entirely by the presence of boric oxide. Undoubtedly the liquid of Asiatic origin is the purer of the two samples in respect of less volatile materials, and this makes it difficult to select the figures which should be employed to arrive at the respective means. This difficulty has been avoided by arbitrarily taking means of (i) the first half, (ii) the first three-quarters, (iii) the middle half: these results are tabulated in Table IX.

TABLE IX.

| | Californian. | Asiatic. | Difference. |
|---|---|---|---|
| (i) | 10·823 | 10·813 | 0·010 |
| (ii) | 10·825 | 10·814 | 0·011 |
| (iii) | 10·830 | 10·817 | 0·013 |

These figures suggest that there is a real difference between the atomic weights of the two samples of boron, although this difference would seem to be less than that previously indicated by the $BCl_3 : 3Ag$ ratio. This discrepancy is explained by the traces of impurity disclosed in the Californian material in the course of the present investigation.

The authors desire to acknowledge a grant from the Department of Scientific and Industrial Research enabling one of them (H.C.S.) to take part in this inquiry, and to express their thanks to Captain F. P. Mills of the Northumberland and Durham Rescue Brigade for kindly supplying the necessary liquid air.

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# XLVI.—*The Ignition of Gases. Part VI. Ignition by Flames. Mixtures of the Paraffins with Air.*

By Noel Stanley Walls and Richard Vernon Wheeler.

One of the objects of the research of which the present paper forms a part has been to determine, more particularly in relation to problems of safety in coal mines, which mixtures of methane (firedamp) and air can be most readily ignited. It has been shown that this question can only be answered fully when the means of ignition are specified, for the answer depends primarily on the nature of the source of ignition.

For example, mixtures containing 5—6% of methane have been found to be the most readily ignited by the walls of a heated chamber into which they are admitted, the temperature required being lowest for these mixtures (J., 1922, **121**, 2079); but when the source of ignition is an electric spark, whether capacity or inductance, mixtures containing 8·25—8·5% are the most readily ignited, the sparks just capable of igniting them having the least energy (J., 1920, **117**, 903; 1925, **127**, 14).

The essential difference between these two sources of ignition lies in their time of contact with the mixture to be ignited, with respect to which they represent extremes, the heated surface being a maintained, and the electric spark a momentary, source of heat. It has been shown that ignition by a heated surface is not instantaneous; at the "ignition-temperature," * the time of contact between the heated surface and the mixture required before inflammation can occur may be many seconds, whilst even at temperatures several hundred degrees higher than the ignition temperature there is a measurable lag on ignition. On the other hand, we have given reasons for believing that the study of the ignition of gases by a momentary source of heat of high temperature should be regarded more as a study of the propagation of flame than of its initiation (J., 1924, **125**, 1858), flame spreading away from the path of an electric discharge most readily in those mixtures in which the speed of propagation normally is fastest.

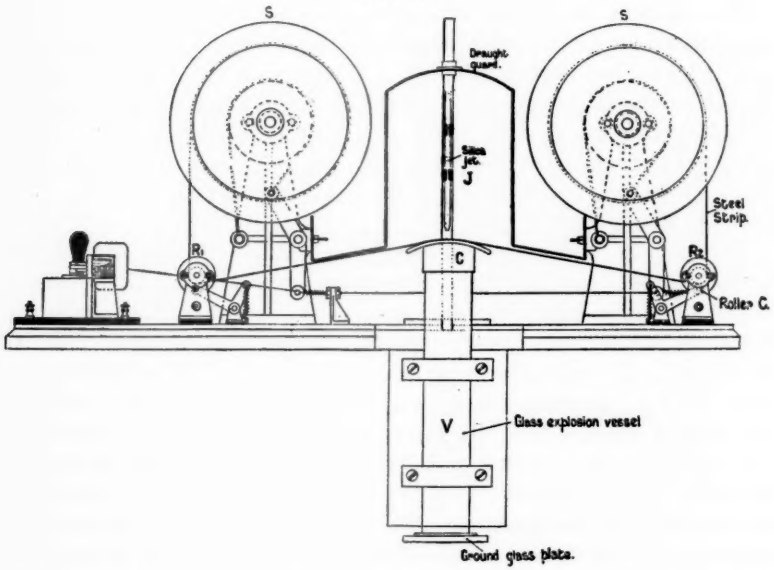
It will be realised that a heated surface, even at a very high temperature, would fail to ignite a gaseous mixture if it did not remain in contact with it beyond the duration of the period of "lag," and it can be understood that any source of ignition of high intensity, *e.g.*, a flame, might fail for the same reason. Flames

* *I.e.*, the lowest temperature, under the conditions of experiment, at which inflammation takes place, no matter how long the surface remains in contact with the mixture.

can, indeed, be projected into explosive mixtures of methane and air without igniting them, a fact which suggested means of determining the relative ignitability of different mixtures of methane and air, for, although any sustained flame is at a temperature sufficiently high to ignite any mixture of methane and air,* it should be possible, by limiting the time of exposure of a flame of given character to different mixtures, to discriminate between them.

Preliminary experiments (Safety in Mines Research Board, Paper No. 24, 1926) showed that the lag on ignition of mixtures

FIG. 1.




of methane and air by flames was sufficiently long to permit of accurate measurement, and that the duration of the lag varied with the composition of the mixture. An apparatus was therefore devised to measure the minimum time of exposure necessary for a flame of standard character to ignite mixtures of known composition. In this way, the relative ignitabilities of different mixtures could be expressed in terms of the duration of the lag on ignition under the conditions of experiment. The apparatus (for details, see "Experimental") consisted of a glass explosion vessel, V (Fig. 1), with a cap of brass, C, over which a thin steel strip could

* A possible exception is the "cool flame" observed in special circumstances, as in a gently-warmed mixture of ether vapour and air.

be rapidly moved. The exposure of the inflammable mixture to a flame playing vertically downwards from a silica jet, J, was effected when a hole, 1 cm. in diameter, in the steel strip coincided with a hole of the same diameter in the brass cap. The duration of exposure was varied by varying the speed of movement of the steel strip.

It was early found that the flame to be used as the source of ignition of a mixture of given composition must be fully aërated, otherwise it would abstract oxygen from the mixture and alter its composition before igniting it. In a series of experiments, *e.g.*, with methane and air, a false idea would thus be given regarding the composition of the most readily ignitable mixture. The flame used for the experiments described in this paper was a fully aërated coal-gas flame.

A close study of the manner in which the flame was exposed to the mixture during these experiments showed that, although its length when burning in still air was sufficient, its tip did not enter the explosion vessel when the hole in the cap was uncovered by the hole in the steel strip. The disturbance of the air caused by the rapidly moving strip caused the tip of the gas-jet to flatten in such a manner that a disc of flame was presented to the mixture. By adjusting the length of the flame when burning in still air, the diameter of the disc of flame exposed to the mixture during an experiment could be varied. With a flame adjusted to be 1 cm. in length, the disc was about half the diameter of the hole in the brass cap of the explosion-vessel; whilst when the jet was 1·5 cm. long the disc spread completely over the area of the hole. Under the latter conditions, it was not easy, with the apparatus as designed, to discriminate between the durations of exposure required to ignite mixtures of methane and air containing between 8 and 12% of methane, but with the smaller disc of flame marked differences could be measured throughout the range of inflammable mixtures.

Experiments were made with methane, ethane, propane, and pentane in admixture, severally, with air.

*Mixtures of Methane and Air.*—The results obtained for the lag on ignition of mixtures of methane and air, using three different sizes of disc of flame as the source of ignition, are in Table I. The recorded areas of the discs of flame are approximate. The measurements actually made to ensure that the area of flame was constant in each series of experiments were of the lengths of the jets when burning in still air.

The general conclusion to be drawn from these results is that the mixtures of methane and air most readily ignited by fully

TABLE I.

*The Ignition of Methane–Air Mixtures by Flames.*

| Flame area: 20 sq. mm. | | Flame area: 45 sq. mm. | | Flame area: 75 sq. mm. | |
|---|---|---|---|---|---|
| Methane, %. | Duration of exposure required for ignition (millisecs.). | Methane, %. | Duration of exposure required for ignition (millisecs.). | Methane, %. | Duration of exposure required for ignition (millisecs.). |
| 7·90 | 12·40 | 7·95 | 6·94 | 7·40 | 7·50 |
| 8·05 | 9·25 | 8·15 | 5·42 | 8·10 | 3·64 |
| 8·20 | 8·75 | 8·20 | 5·12 | 8·45 | 3·62 |
| 8·65 | 7·90 | 9·35 | 4·38 | 9·15 | 3·61 |
| 8·70 | 7·81 | 10·80 | 4·50 | 9·95 | 3·53 |
| 9·05 | 7·37 | 12·70 | 7·50 | 10·70 | 3·56 |
| 9·65 | 6·90 | | | 11·10 | 3·62 |
| 10·30 | 6·90 | | | 12·05 | 3·60 |
| 10·85 | 7·12 | | | 12·15 | 3·63 |
| | | | | 12·70 | 6·69 |

aërated flames, inasmuch as the time of contact required is shortest, contain 9·5—10·0% of methane.*

The duration of exposure required for ignition to occur, as might be expected, is less the larger the area of the flame used as the source of ignition; whilst, under the conditions of these experiments, the larger the area of the igniting flame the less marked is the differentiation between one mixture and another.

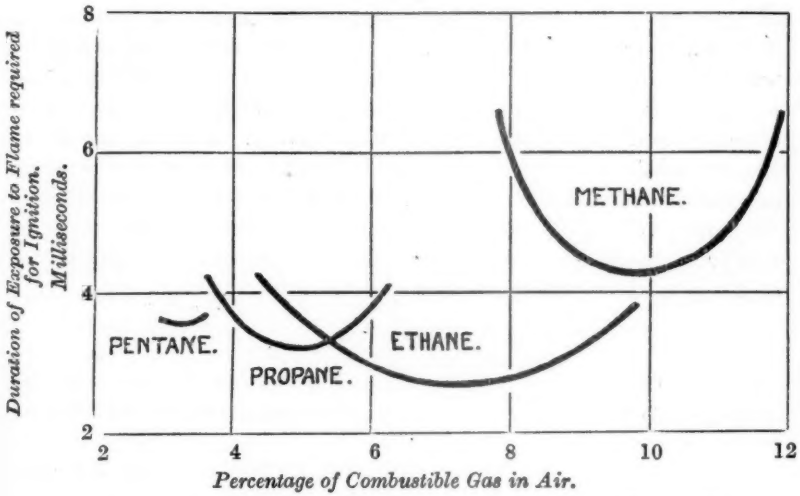
*Mixtures of the Higher Paraffins and Air.*—There was considerable difficulty throughout this research in maintaining such constancy of experimental conditions as would ensure that the results recorded were strictly comparable one with another, and frequent check experiments with a given mixture, adopted as standard, were necessary. In particular, great care had to be taken to avoid disturbing the position of the silica nozzle at which the igniting flame was produced, for the character of the flame as presented to the mixture to be ignited was thereby altered. If this occurred during a series of experiments, it usually saved time to start the series afresh rather than to attempt to reproduce previous conditions.

The results recorded in Table I for mixtures of methane and air were all obtained under strictly comparable conditions of experiment, but when attempting to continue the series to include the ignition of other paraffins we were not so fortunate. We have determined, however, in individual series not comparable one with another,

* In earlier experiments, when an under-aërated flame was used, the mixtures containing the lower percentages of methane appeared to be more readily ignitable, for the reason already given. A similar effect has been observed during experiments on the ignition of mixtures of methane and air by heated wires when the wire has been of a readily oxidisable metal.

the most readily ignitable mixtures of ethane, propane, and pentane, respectively, with air. We have also obtained relative values, under standard conditions, for the duration of exposure to a fully aërated flame required for the ignition of each of these most readily ignitable mixtures. From these data, curves can be constructed relating percentages of each combustible gas in air with the time of exposure to a standard flame required to ignite them, and each curve can be assigned its proper position relative to the others. Such curves are reproduced in Fig. 2.

FIG. 2.




The composition of the most readily ignitable mixture in each instance corresponds fairly closely with that of the mixture in which the initial speed of propagation of flame is most rapid. The values are recorded in Table II.

TABLE II.

| Combustible gas. | Mixture in which speed of uniform movement of flame is fastest. (Combustible gas, %.) | Relative speed of flame (cm./sec.).* | Mixture most readily ignited by flame. (Combustible gas, %.) | Relative duration of exposure of flame required (millisecs.). |
|---|---|---|---|---|
| Methane ..... | 9·65 | 91 | 9·8—10·0 | 4·3 |
| Ethane ..... | 6·05 | 127 | 6·8— 7·0 | 2·7 |
| Propane ..... | 4·45 | 114 | 4·8— 5·0 | 3·2 |
| *n*-Pentane ..... | 2·90 | 115 | 3·1— 3·3 | 3·5 |

* In a horizontal brass tube 5 cm. in diameter (Mason, J., 1923, **123**, 210).

The deduction to be drawn from these results is that the ease of ignition of an explosive mixture by a momentary source of heat is dependent essentially on the normal speed of propagation of flame in the mixture. Ease of "ignition," therefore, here corresponds with the ability of the flame to travel through the mixture after the source of ignition has been removed. This is the same deduction as was drawn with respect to ignition by the impulsive electrical discharge, and a similar explanation, *viz.*, that a certain minimum volume of an explosive mixture must be burnt in order that there shall be a spreading inflammation through it, can be advanced.

There is thus a marked resemblance between the phenomena of ignition of the paraffin hydrocarbons by means of momentary flames and by means of electric sparks. The resemblance persists when the effect of increasing the area of flame momentarily exposed to the mixtures (see Table I) is compared with the behaviour of capacity and inductance sparks, respectively. Just as increasing the area of the flame renders it more difficult to differentiate between one mixture and another with respect to its ignitability, so does the larger volume of inductance sparks, as compared with capacity sparks, have the effect of masking small differences in the ignitability of those mixtures that are most readily ignited.

## Experimental.

Details of the apparatus used for bringing the various mixtures into contact with a flame during a measured small interval of time are as follows.

The steel strip (Fig. 1) was 0·05 mm. in thickness and 3·81 cm. broad. It was wound by means of an electric motor from one spool, S, to another under rollers, $R_1$ and $R_2$, between which the explosion vessel was mounted. Arrangements were made whereby the speed of movement of the strip could be accurately measured and, to avoid accidents due to overwinding, its movement automatically stopped a short time after the exposure of the mixture in the explosion-vessel to the jet of flame.

The explosion-vessel was 5·5 cm. in diameter and 50 cm. long. Its upper end was closed by the brass cap, C, as already explained, and the lower end could be closed by a ground-glass cover-plate whilst the mixture to be tested was being introduced. This was done by exhaustion of the air through a tap at the side and its replacement by a mixture of known composition previously prepared in a gas-holder. The hole in the brass cap, which was 1·5 mm. thick, had its lower edge brought to a thin bevel.

In carrying out an experiment, the speed of movement of the steel strip, from which the time of exposure of the flame to the

mixture could be calculated, was adjusted roughly so that ignition of the mixture did not occur, and then a series of trials was made with carefully regulated speeds so as to determine accurately the duration of exposure necessary for ignition. The measurements of duration of exposure had a maximum error of 0·012 millisec.

This work has been carried out for the Safety in Mines Research Board, to whom our thanks are due for permission to publish.

THE UNIVERSITY, SHEFFIELD. [*Received, August 31st*, 1926.]

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## XLVII.—*The Combustion of Complex Gaseous Mixtures. Part III. The Inflammation of Mixtures of Carbon Monoxide and Hydrogen with Air in a Closed Vessel.*

By GEORGE BARTON MAXWELL, WILLIAM PAYMAN, and RICHARD VERNON WHEELER.

IN Part II of this research (J., 1923, **123**, 1251) reference was made to preliminary experiments on the inflammation of mixtures of carbon monoxide and hydrogen with air, ignited at the centre of a spherical vessel, and some of the results were quoted to show that the "law of speeds" * would apply to the spread of flame in complex gaseous mixtures ignited under such conditions. In the present paper further series of experiments of a like nature are described.

Few measurements by earlier investigators are available of the magnitude and rate of development of pressure when mixtures of carbon monoxide or hydrogen with air are inflamed in closed vessels. Langen's experiments with these gases ("Mitteilungen über Forschungsarbeiten aus dem Gebiete des Ingenieurwesens," **8**, 1903) were chiefly with mixtures with pure oxygen, and he was only concerned with measuring the maximum pressures. The rate of development of pressure, under the same conditions of experiment, was examined by Nägel (*ibid.*, **54**, 1908) for hydrogen, but he chose only mixtures containing excess of oxygen. Both Langen and Nägel used a spherical vessel of 34 litres capacity, and ignited their mixtures by an electric spark passed at the centre.

Bone and Haward (*Proc. Roy. Soc.*, 1922, **100**, 67) and Bone,

* "Given two or more mixtures of air or oxygen with different individual gases, in each of which the speed of propagation of flame is the same, all combinations of the mixtures, of the same type, propagate flame at the same speed, under the same conditions of experiment" (J., 1922, **121**, 365).

Newitt, and Townend (J., 1923, **123**, 2008) have made measurements of the pressures produced and their rate of development with hydrogen–air and carbon monoxide–air mixtures at various initial pressures up to 50 atm. Their explosion-vessel was spherical, and their source of ignition, a heated platinum wire, was near the wall. Under these conditions, part of the flame is in contact with the wall of the vessel whilst the remainder is travelling through the mixture, so that heat is lost by conduction before the maximum pressure is attained; on the other hand, with central ignition, except when the speed of the flame is very slow, the flame does not reach the boundary of the vessel until the whole of the mixture has been inflamed, *i.e.*, until the instant of maximum pressure.

Crowe and Newey (*Phil. Mag.*, 1925, **49**, 1112) have carried out experiments with mixtures of carbon monoxide and air ignited centrally in a sphere of 40·6 cm. diameter. They have, however, disregarded the effect of water vapour on the rate of combustion of carbon monoxide, and their results are consequently difficult to interpret. Fenning (*Phil. Trans.*, 1926, *A*, **225**, 331) ignited mixtures of carbon monoxide and air, hydrogen and air, and blends of the two mixtures, at the centre of a cylindrical explosion-vessel, 20 cm. long and 18 cm. in diameter, at an initial pressure of 5·2 atm. and an initial temperature of 50°. He also studied the effect of water vapour on the rate of explosion of carbon monoxide.

For the experiments now described, new apparatus was constructed, the general arrangement of which is shown in Fig. 1. The principal new feature was a manometer of the Petavel type, designed to obtain as accurate a measure as possible of the rate of development of pressure with explosions that varied considerably in this respect. The gauge consisted essentially of a steel piston 5 cm. in diameter, screwed into the free end of a tubular steel spring, S. The other end of the spring was attached rigidly to a brass casing, C, which screwed on to the explosion-vessel. When assembled, the face of the manometer piston was flush with the inner wall of the explosion-vessel. Any movement of the piston caused a compression of the spring, which was transmitted, by a steel connecting-rod, R, to a small concave mirror, M, of stainless steel. One end of the connecting-rod was screwed into the piston, whilst the mirror rested in a slot in the other end and was held in position by taut stays of piano-wire, W. Considerable difficulty had been experienced with a previous example of this type of manometer, used in our preliminary experiments, in arranging that it should be equally sensitive in registering explosions of very slow and very rapid development. In the present example, the clearance between the piston and a brass bush which is screwed

FIG. 1.

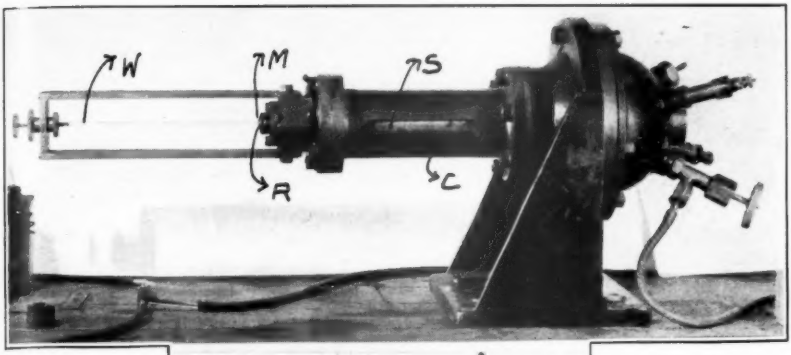
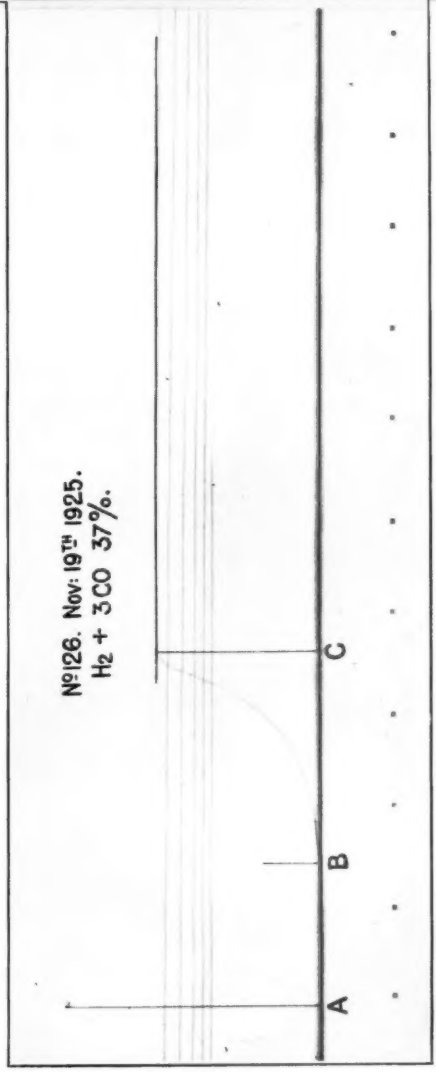



FIG. 2.




[*To face page* 298.]

into the wall of the bomb was exceedingly small, and, unless the piston was frequently removed and carefully cleaned, there was a danger that a film of moisture would form on its periphery. This would cause a frictional force resisting the free movement of the piston. Strict attention has been paid to this point throughout our experiments.

The explosion-vessel was a spherical bomb of 4 litres capacity, fitted with a valve and firing electrodes, similar to that used in earlier work (J., 1918, **113**, 854). A rubber washer between the spring of the manometer and a seating in the wall of the bomb made a gas-tight joint.

A rise in pressure within the explosion-vessel of 1 atm. caused a movement of the piston of 0·0012 mm. This movement was magnified by an optical lever. A beam of light, reflected from the mirror, was focussed on the surface of a strip of sensitised paper carried by a revolving drum. The source of illumination of the mirror was a carbon arc-lamp. The moment of ignition of the mixture was recorded on the sensitised paper by focussing on it, through a telescope, the spark from a gap in series with the spark-gap at the centre of the explosion-vessel. This latter was between pointed electrodes of copper, 3 mm. apart. The spark used to cause ignition was, throughout the experiments, the secondary discharge from a 6-inch induction-coil, using a current of 10 amps. through the primary circuit, the trembler being locked. The rate of revolution of the camera drum was recorded by photographing on it the sparks produced at the mercury contact of an electrically driven tuning-fork, of 100 frequency. A typical record (reduced in size to nearly one-half for reproduction) is shown in Fig. 2. On this record, A is the time of ignition; B, the time of first appearance of pressure; and C, the time of attainment of maximum pressure. The record of the tuning-fork, marking 1/100ths of a second, appears at the bottom of the chart. The speed of revolution of the recording drum was varied according to the rapidity of the explosion. With the most rapid explosions, those of mixtures of hydrogen and air, it was such that a time-interval of 0·01 sec. measured 4·5 cm. on the chart.

Each gas mixture was prepared in a 20-litre glass gas-holder and analysed before use. In each experiment, the bomb was exhausted of air to within a few mm. of mercury, filled with the mixture to be experimented with, re-exhausted, and refilled. The results, both for maximum pressures attained and for rates of development of these pressures, have been checked by explosions of similar mixtures in a bomb of the same dimensions fitted with a different type of manometer. Details of these check experiments, together

with the records of pressures, will be given in a later communication. The present paper deals only with the rate of development of pressure.

The main object of the present series of experiments has been to test the application of the law of speeds to the rate of development of pressure when complex gaseous mixtures are ignited in a closed vessel. With this object in view, a series of mixtures has been used of air with hydrogen and carbon monoxide, both individually and also jointly in the proportions corresponding to $3H_2 + CO$, $H_2 + CO$, and $H_2 + 3CO$. Since these experiments also throw light on the effect of water vapour on the combustion of carbon monoxide, a further series of experiments has been made with mixtures of carbon monoxide and air saturated with water vapour at different temperatures. Unless otherwise stated, the mixtures were initially at atmospheric pressure.

### *Rate of Development of Pressure.*

The values obtained for the rate of development of pressure on explosion of the various mixtures, all saturated with water vapour at 15°, are given in Table I, in which the percentage given in col. 1 relates to the inflammable gas shown at the head of each sub-section.

TABLE I.

*The Rate of Development of Pressure. Hydrogen, Carbon Monoxide, and Mixtures of the Two with Air. (Saturated with water vapour at 15° and atmospheric pressure.)*

| Inflammable gas, %. | Time between ignition and first appearance of pressure (sec.). | Time between ignition and maximum pressure $t$ (sec.). | $1/t$. | Mean speed of flame (cm./sec.). |
|---|---|---|---|---|
| | | (*a*) Hydrogen. | | |
| 10·2 | 0·070 | 0·166 | 6·0 | 58 |
| 15·1 | 0·019 | 0·038 | 26·3 | 260 |
| 19·4 | 0·009 | 0·019 | 52·6 | 510 |
| 24·5 | 0·005 | 0·011 | 90·9 | 880 |
| 28·9 | 0·003 | 0·008 | 125 | 1220 |
| 34·1 | 0·003 | 0·007 | 143 | 1390 |
| 37·2 | 0·003 | 0·007 | 143 | 1390 |
| 39·3 | 0·003 | 0·007 | 143 | 1390 |
| 44·4 | 0·003 | 0·008 | 125 | 1220 |
| 45·8 | 0·004 | 0·008 | 125 | 1220 |
| 49·0 | 0·005 | 0·010 | 100 | 970 |
| 54·0 | 0·005 | 0·011 | 90·9 | 880 |
| 56·2 | 0·006 | 0·013 | 76·9 | 750 |
| 57·2 | 0·006 | 0·015 | 66·9 | 650 |
| 62·3 | 0·009 | 0·020 | 50·0 | 440 |
| 66·1 | 0·018 | 0·033 | 30·3 | 290 |

TABLE I (*continued*).

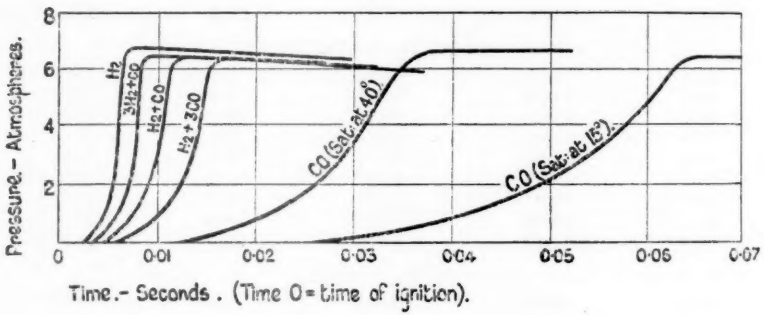
| Inflammable gas, %. | Time between ignition and first appearance of pressure (sec.). | Time between ignition and maximum pressure $t$ (sec.). | $1/t$. | Mean speed of flame (cm./sec.). |
|---|---|---|---|---|
| | | (*b*) $3H_2 + CO$. | | |
| 14·4 | 0·036 | 0·072 | 13·9 | 130 |
| 20·0 | 0·012 | 0·026 | 38·5 | 370 |
| 24·0 | 0·007 | 0·016 | 62·5 | 610 |
| 29·2 | 0·006 | 0·011 | 90·9 | 880 |
| 37·7 | 0·004 | 0·009 | 111 | 1080 |
| 43·7 | 0·004 | 0·009 | 111 | 1080 |
| 51·0 | 0·006 | 0·013 | 76·9 | 750 |
| 56·5 | 0·007 | 0·016 | 62·5 | 610 |
| 64·6 | 0·020 | 0·041 | 24·4 | 240 |
| | | (*c*) $H_2 + CO$. | | |
| 15·8 | 0·037 | 0·095 | 10·5 | 100 |
| 18·0 | 0·024 | 0·078 | 12·8 | 120 |
| 24·0 | 0·009 | 0·026 | 38·5 | 370 |
| 28·9 | 0·006 | 0·017 | 58·8 | 570 |
| 33·3 | 0·005 | 0·013 | 76·9 | 750 |
| 38·9 | 0·005 | 0·012 | 83·3 | 810 |
| 43·4 | 0·004 | 0·012 | 83·3 | 810 |
| 56·1 | 0·006 | 0·017 | 58·8 | 570 |
| 60·8 | 0·017 | 0·030 | 33·3 | 320 |
| | | (*d*) $H_2 + 3CO$. | | |
| 15·9 | 0·056 | 0·017 | 5·9 | 58 |
| 21·0 | 0·023 | 0·062 | 16·1 | 160 |
| 26·8 | 0·012 | 0·032 | 31·1 | 300 |
| 30·0 | 0·009 | 0·025 | 40·9 | 390 |
| 37·0 | 0·007 | 0·018 | 55·6 | 540 |
| 39·3 | 0·007 | 0·017 | 58·8 | 570 |
| 46·3 | 0·007 | 0·017 | 58·8 | 570 |
| 49·1 | 0·007 | 0·018 | 55·6 | 540 |
| 57·6 | 0·012 | 0·029 | 34·5 | 340 |
| 60·7 | 0·019 | 0·045 | 22·2 | 220 |
| | | (*e*) Carbon Monoxide. | | |
| 21·6 | 0·050 | 0·159 | 6·3 | 60 |
| 23·5 | 0·050 | 0·144 | 16·9 | 65 |
| 28·0 | 0·029 | 0·087 | 11·5 | 110 |
| 31·1 | 0·026 | 0·067 | 14·9 | 145 |
| 36·6 | 0·027 | 0·065 | 15·4 | 150 |
| 39·4 | 0·027 | 0·071 | 14·2 | 135 |
| 44·9 | 0·025 | 0·065 | 15·4 | 150 |
| 49·6 | 0·023 | 0·065 | 15·4 | 150 |
| 54·7 | 0·032 | 0·078 | 12·8 | 125 |

Time–pressure curves, reproduced from the records, for each of the maximum-speed mixtures [*i.e.*, those mixtures of inflammable gas and air (or oxygen) in which the proportions of inflammable gas are such that the speed of flame in the mixture, under given experimental conditions, is the fastest obtainable] are shown in Fig. 3 plotted on the same time-scale to enable direct comparison to be made. The curves form a continuous series, of the same

general character, from the slow carbon monoxide–air explosion to the comparatively rapid hydrogen–air explosion.

Strictly speaking, the measure of the "rate of development of pressure" should be the increment of pressure per unit of time. Since, however, this is continuously changing from one instant to the next, it is usual to regard the rate of development as the rate at which the maximum pressure is reached. For convenience, the time between the moment of ignition and that of attainment of maximum pressure (time of explosion, $t$) is actually measured, but the rate of development of pressure is given by the reciprocal of this time, $1/t$.

FIG. 3.




When ignition takes place at the centre of a spherical vessel, the moment of attainment of maximum pressure synchronises with the moment at which the flame reaches the walls.* Hence the

* Unless the speed of the flame is very slow. This was proved by Wheeler (J., 1918, **113**, 840) for mixtures of methane and air containing 7—11% of methane, by recording the time of fusion of screen wires (tinned copper wire of 0·025 mm. diameter) carrying an electric current and stretched near the wall of the explosion-vessel at a measured distance from the spark-gap. A similar method has been used in the present research, using mixtures of carbon monoxide and air, with the following results:

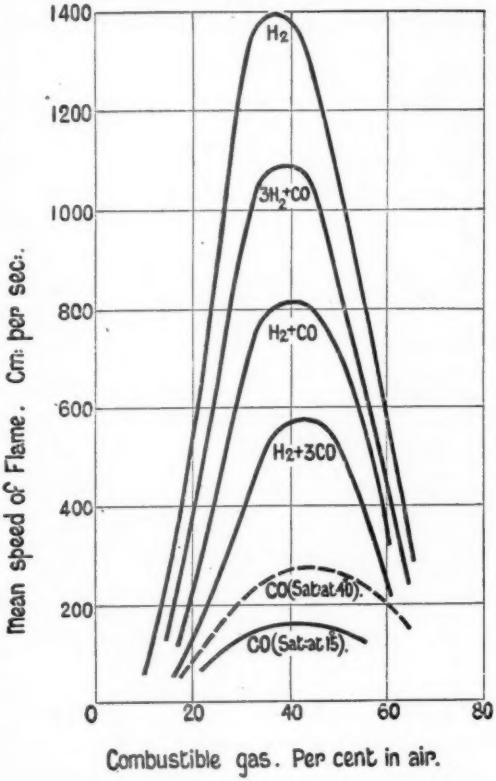
| CO (%). | Time from ignition to maximum pressure (sec.). | Time taken for flame to reach wall of explosion-vessel (sec.). |
|---|---|---|
| | (*a*) Mixtures dried by calcium chloride. | |
| 30·5 | 0·129 | 0·128 |
| 33·1 | 0·122 | 0·121 |
| 40·0 | 0·115 | 0·113 |
| 45·8 | 0·121 | 0·119 |
| | (*b*) Mixtures saturated with water vapour at 15°. | |
| 23·5 | 0·144 | 0·142 |
| 28·0 | 0·087 | 0·082 |
| 49·6 | 0·065 | 0·066 |

The times correspond within the limits of error of measurement of the speeds of the flames by the screen-wire method.

mean speed of the flame during its passage from the centre to the sides gives a direct measure of the "rate of development of pressure" as defined in the previous paragraph. This mean speed is $r/t$, where $r$ is the radius of the sphere, which was 9·73 cm. in the present experiments. The equivalent value was used by Nägel (*loc. cit.*) for recording his results.

In Fig. 4, the rates of development of pressure are plotted against the compositions of the mixtures with air of $H_2$, $3H_2 + CO$, $H_2 + CO$, $H_2 + 3CO$, and CO. The dependence of the rate of development of pressure on the speed of the flame will be apparent if Fig. 4 be compared with Fig. 5, which records the speeds of propagation of flame during the uniform movement in a horizontal glass tube 2·5 cm. in diameter, the speeds being plotted against the compositions of the same series of mixtures as has been used in the present research. The mean speed of the flame in the sphere is about 2½ times as great as that of the uniform movement in the glass tube.

FIG. 4.



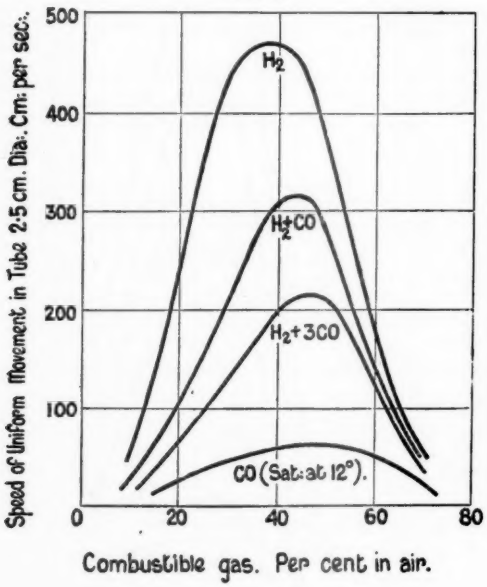

### *Application of the Law of Speeds.*

To simplify the application of the law of speeds to the results recorded in Table I, those obtained with mixtures of carbon monoxide and air are not used in the first calculations, but are reserved until the effect of water vapour on the rate of development of pressure in carbon monoxide–air mixtures has been discussed. Instead of using hydrogen and carbon monoxide, therefore, as the two "standard" gases, hydrogen and the mixture

($H_2 + 3CO$) are used. Two vols. of hydrogen mixed with 1 vol. of ($H_2 + 3CO$) will yield a mixture of composition $3H_2 + CO$, whilst 1 vol. of hydrogen mixed with 2 vols. of ($H_2 + 3CO$) will yield a mixture of composition $H_2 + CO$.

The results of the calculations are shown in Fig. 6. In preparing this diagram, the times of explosion were first plotted against the compositions of the mixtures used as "standard." These curves are shown as continuous lines. From these curves, the "theoretical curves" for the mixtures $3H_2 + CO$ and $H_2 + CO$ were calculated by means of the law of speeds and are shown in the diagram in broken line. The values found experimentally were added to the diagram later. They show satisfactory agreement between observed and calculated values. Only the lower portions of the curves are shown in the diagram, since inclusion of all values found would have necessitated an excessive lengthening of the time scale.

FIG. 5.



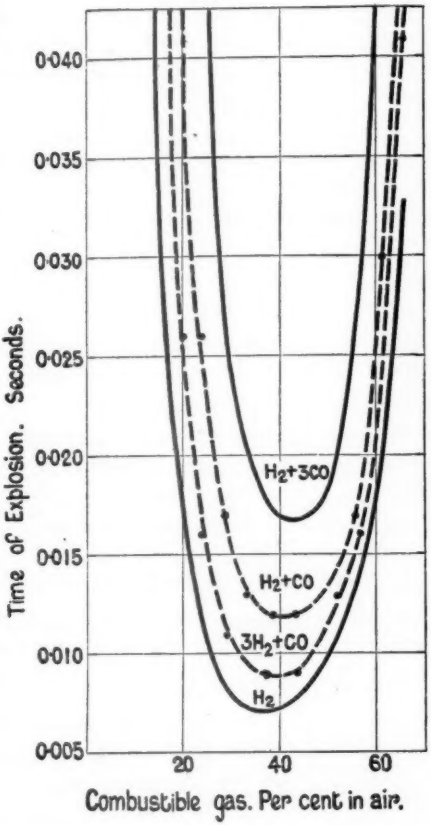

*The Effect of Water Vapour on the Combustion of Carbon Monoxide.*

In Part II of this series of papers (*loc. cit.*, p. 1252) it was shown that the speed of the uniform movement of flame in mixtures of carbon monoxide and air varied with the proportion of water vapour present. Some doubt, therefore, existed as to the correct value to use for the speed of flame in mixtures of carbon monoxide and air when attempting to calculate, by means of the law of speeds, the speed of flame in complex mixtures containing carbon monoxide, unless the degree of saturation of the complex mixture by water vapour was known. It was shown, however, that when hydrogen, or an inflammable gas containing hydrogen, was present in the complex mixture in more than quite a small proportion, the speed of flame became independent of the concentration of water vapour,

so that the speed of flame in such a complex mixture could be used as a basis from which an " effective " speed of flame in the mixtures of carbon monoxide and air could be calculated, and the value thus obtained could be used for further calculations. An alternative method for determining the " effective " speed of flame in a given mixture of carbon monoxide and air was described, this speed being the maximum obtainable with that mixture with the concentration of water vapour that had the optimum effect.

The same argument applies to the rate of development of pressure in complex mixtures of inflammable gases, containing carbon monoxide, ignited centrally in a spherical vessel. We have tested it experimentally, using a " maximum-speed mixture " of carbon monoxide and air, containing 48% of carbon monoxide, the amount of water vapour present being varied by varying the saturation-temperature. The explosion-vessel was installed within a heat-insulated wooden box, which also contained electric heater lamps. The pressure-gauge mirror and a portion of the gauge itself protruded from the enclosure.

FIG. 6.




The charge density was kept constant in these experiments, the bomb being filled at 15° and closed before being heated to the desired temperature. Sufficient water to ensure saturation at the experimental temperature was introduced into the bomb before filling it with the explosive mixture. The results are shown in Table II.

Time–pressure curves are reproduced in Fig. 7.

It will be seen that the rate of development of pressure tended towards a maximum when 6—7% of water vapour was present.

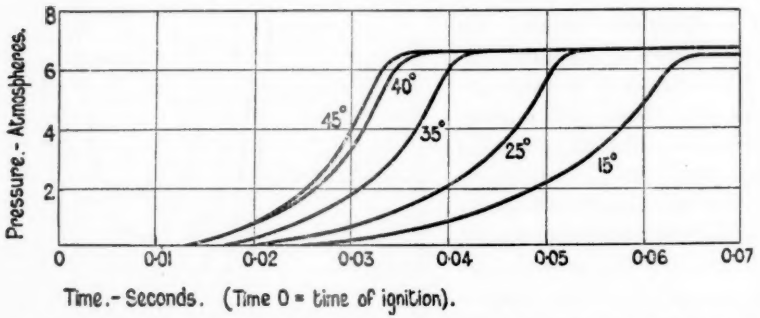
TABLE II.

*The Influence of Water Vapour on the Rate of Development of Pressure in a Mixture of Carbon Monoxide and Air.* (48% CO.)

| Saturation temp. | Water vapour (% by vol.). | Time between ignition and first appearance of pressure (sec.). | Time between ignition and maximum pressure (sec.). |
|---|---|---|---|
| 15° | 1·7 | 0·025 | 0·065 |
| 25 | 2·9 | 0·020 | 0·053 |
| 35 | 4·8 | 0·017 | 0·043 |
| 40 | 6·2 | 0·012 | 0·038 |
| 45 | 7·9 | 0·014 | 0·037 |
| 50 | 9·7 | 0·014 | 0·038 |
| 55 | 12·0 | 0·015 | 0·037 |
| 65 | 17·3 | 0·015 | 0·037 |

This is rather more than is required to develop the maximum speed during the uniform movement of flame, when the explosive mixture is initially at atmospheric pressure.

FIG. 7.




*Pressure development. Mixtures of carbon monoxide and air saturated with water vapour at different temperatures.*

The value so obtained, 0·037 sec., for the "effective" time of explosion in the maximum-speed mixture of carbon monoxide and air, was now used as the standard, together with the corresponding value for the maximum-speed mixture of hydrogen and air, to calculate the times of explosion for the three mixtures $3H_2 + CO$, $H_2 + CO$, and $H_2 + 3CO$. The results are recorded, and compared with the experimentally determined values, in Table III.

TABLE III.

| Inflammable gas ..... | $H_2$. | $3H_2+CO$. | $H_2+CO$. | $H_2+3CO$. | CO. |
|---|---|---|---|---|---|
| Time of explosion (calc.) (sec.) | — | 0·009 | 0·012 | 0·018 | — |
| „ „ (obs.) „ | 0·007 | 0·009 | 0·012 | 0·017 | 0·037 |

The close agreement between the observed and calculated values affords decisive proof of the assumption that the "effective speed"

of combustion of carbon monoxide is developed when a sufficient quantity of hydrogen is mixed with it, just as it is when a sufficiency of water vapour is present.

We pointed out, in our previous paper, that the results obtained by Bone and Haward (*loc. cit.*) for the rate of development of pressure in explosions of mixtures of carbon monoxide and hydrogen with air—results which the authors deemed to require an abnormal explanation—could be explained by the law of speeds. Bone, Newitt, and Townend (*loc. cit.*) have not accepted our explanation, regarding as "wholly fanciful" the assumption with regard to the "effective speed" of combustion of carbon monoxide which we have now proved to be correct, and have recorded the results of experiments intended to disprove it. Briefly, they have found that in certain explosions of the mixture $2CO + O_2 + 4N_2$, fired at an initial pressure of 50 atm., and at an initial temperature of 17—23·1°, what they term "the time in seconds taken for the attainment of maximum pressure" did not vary much whether the mixture were "dry," "undried," "moist," or "wet." Thus, they say: "There is practically no difference between the 'dry' and either the 'moist' or the 'wet' series; for in all these cases it amounted as nearly as may be to 0·18 second. In the 'undried' series (that is, when the water vapour present would probably not much exceed 1 in 2000) the time was somewhat shorter, namely, 0·13 to 0·15 second. It therefore seems clear that the presence of a very much smaller amount of water vapour sufficed to produce the optimum combustion conditions in our said experiments than was found necessary either by H. B. Dixon for the fastest propagation of detonation through $2CO + O_2$ mixtures at ordinary pressures, or by Payman and Wheeler for the fastest inflammation of carbon monoxide–air mixtures also at atmospheric pressure."

Apparently, the assumption is made that the amount of water vapour required to produce the optimum combustion conditions in their experiments was attained with the "undried" mixtures and had been passed with the "moist" and the "wet." Assuming that in the "wet" experiments the gases were saturated at the initial temperature and pressure (23·1° and 50 atm.), there could have been no more than 0·06% of water vapour present. In view of the fact that, under similar conditions of combustion, the concentration of water vapour found to be most effective lies between 6 and 7%, the speed of flame in a given mixture of carbon monoxide and air being then nearly four times as great as when the mixture is roughly dried, it is not surprising that Bone, Newitt, and Townend noticed very little difference between their series of experiments.

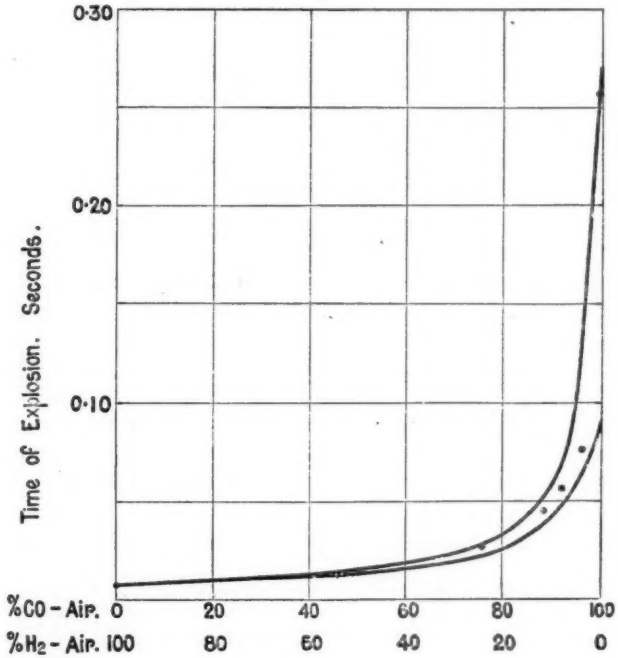
On the other hand, the smallest proportion of hydrogen in the mixture used by Bone and Haward was 1·2% (in the mixture $1/12H_2 + 23/12CO + O_2 + 4N_2$), or 20 times as much as the greatest proportion of water vapour in the mixtures used by Bone, Newitt, and Townend, whose experiments, therefore, yield no information regarding the relative influence of water vapour and hydrogen upon the explosion of carbon monoxide–air mixtures at high pressures. It may here be pointed out that although the times given by these authors are recorded as the times taken for "the attainment of maximum pressure," they are actually the times that elapsed between (*a*) the first indication of a rise above the initial pressure and (*b*) the attainment of the maximum, for they did not determine the time of ignition. There is no evidence that the interval that elapsed between ignition and the first appearance of pressure was negligible in their experiments or was the same in every one of the series. There is ample evidence that, in the explosion of mixtures initially at atmospheric pressure, this interval is of considerable importance.

Confirmation of our results is given by the work of Fenning (*loc. cit.*), who measured the time taken from the moment of ignition to the moment of attainment of maximum pressure in explosions (at an initial pressure of 5·2 atm. and an initial temperature of 50°) with a series of mixtures similar to those used by Bone and Haward. In discussing the results of his experiments, Fenning comments on the marked effect of a small proportion of hydrogen on the rapidity of explosion of a carbon monoxide–air mixture. The effect could have been calculated from the law of speeds in the following manner: Under the conditions of Fenning's experiments, the shortest time of explosion of the mixture $2CO + O_2 + 3{\cdot}8N_2$, *viz.*, 0·0901 sec., was obtained when the mixture was completely saturated with water vapour, when it contained 2·38% by volume. The time of explosion with a "comparatively dry" mixture of the same composition (containing less than 0·05% of water vapour) was 0·2693 sec. The time of explosion of a mixture $2H_2 + O_2 + 3{\cdot}8N_2$ was 0·0074 sec. From these values, the times of explosion for blends of the hydrogen–air and carbon monoxide–air mixtures can be calculated by the law of speeds, using alternatively the value for the "comparatively dry" and the "saturated" carbon monoxide–air mixture. The calculations are shown graphically in Fig. 8, in which the times of explosion are plotted against the compositions of the blends, the upper and lower curves being obtained when the values for the times of explosion in the dry and saturated carbon monoxide–air mixtures, respectively, are used. It is clear that the times of explosion of the blends used by Fenning

should lie on a curve intermediate between the two calculated curves. That they do so is shown in the diagram by the insertion of his experimental values (*loc. cit.*, p. 351) as points.

To emphasise the importance of the presence of water vapour on the rate of development of pressure on explosion of mixtures of carbon monoxide and air, three series of experiments have been carried out, each covering a full range of mixtures between the limits of inflammability, with different concentrations of water vapour in each series. For the first series, the mixtures were roughly

FIG. 8.




dried by passing them through calcium chloride tubes. For the second, they were saturated with water vapour at 15°, the results being recorded in Table I. For the third, they were saturated with water vapour at 40°, this being the temperature at which the optimum effect is produced. The values for the mean speeds of flame obtained in the last series of experiments may be taken as the "effective" values for the rate of development of pressure in carbon monoxide–air mixtures. They have been plotted as a broken line in Fig. 4. The results of the first and third series of experiments are recorded in Table IV.

TABLE IV.

*The Rate of Development of Pressure. Mixtures of Carbon Monoxide and Air.*

| Carbon monoxide, %. | Time between ignition and first appearance of pressure (sec.). | Time between ignition and maximum pressure, $t$ (sec.). | $1/t$. | Mean speed of flame (cm./sec.). |
|---|---|---|---|---|
| | (*a*) Mixtures dried by calcium chloride. | | | |
| 19·4 | 0·105 | 0·337 | 3·0 | 30 |
| 24·9 | 0·054 | 0·150 | 6·7 | 65 |
| 30·5 | 0·048 | 0·129 | 7·7 | 75 |
| 33·1 | 0·050 | 0·122 | 8·2 | 80 |
| 40·0 | 0·042 | 0·115 | 8·7 | 85 |
| 45·8 | 0·046 | 0·121 | 8·3 | 80 |
| 49·6 | 0·048 | 0·136 | 7·3 | 70 |
| | (*b*) Mixtures saturated with water vapour at 40°. | | | |
| 18·4 | 0·063 | 0·218 | 4·6 | 40 |
| 21·8 | 0·038 | 0·096 | 10·4 | 100 |
| 23·7 | 0·035 | 0·080 | 12·5 | 120 |
| 24·1 | 0·030 | 0·076 | 13·2 | 130 |
| 26·7 | 0·027 | 0·058 | 17·2 | 170 |
| 31·0 | 0·018 | 0·047 | 21·3 | 210 |
| 34·5 | 0·014 | 0·041 | 24·4 | 240 |
| 38·3 | 0·014 | 0·038 | 26·3 | 260 |
| 46·1 | 0·014 | 0·037 | 27·0 | 270 |
| 48·3 | 0·013 | 0·038 | 26·3 | 260 |
| 53·3 | 0·015 | 0·040 | 25·0 | 250 |
| 59·1 | 0·017 | 0·045 | 22·0 | 220 |
| 64·3 | 0·023 | 0·062 | 16·1 | 160 |

The experiments recorded in this paper form part of a research that we are carrying out for the Safety in Mines Research Board, to whom our thanks are due for permission to utilise the results.

DEPARTMENT OF FUEL TECHNOLOGY,
SHEFFIELD UNIVERSITY. [*Received, September 11th*, 1926.]

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## XLVIII.—*The Movement of Flame in Closed Vessels: After-Burning.*

By OLIVER COLIGNY DE CHAMPFLEUR ELLIS and RICHARD VERNON WHEELER.

WHEN an explosive gaseous mixture is ignited at some point within a closed vessel, the speed at which the flame begins to spread * is compounded of the speed at which the inflammation is propagated, *i.e.*, is communicated from layer to layer of the mixture, and the speed at which the portion of the mixture about to be burnt moves

* The effect of any initial impetus that may be given by the source of ignition employed is here ignored.

under the expansive force of the portion already burning. Unless the speed of propagation of flame is very rapid, or the vessel very small, the unburnt mixture ahead of the flame-front at first moves freely without being appreciably compressed. A time comes, however, when, owing to the nearness of the walls of the vessel, the unburnt mixture ahead of the flame-front can no longer move freely. Its movement slackens until it ceases, the whole of the mixture between the flame-front and the walls of the vessel being compressed meanwhile, and, eventually, the direction of movement tends to be reversed. The movement of the flame is affected by this slackening of movement of the unburnt mixture, an appreciable retardation of its speed occurring as the walls of the vessel are approached (see *Fuel*, 1925, **4**, 356).

This behaviour of the flame is illustrated in Fig. 1, Plate I, which shows a photographic record, taken on a rapidly revolving drum, of the flame in a 58·4% mixture of carbon monoxide and air moving away from the point of ignition at the centre of a sphere of glass, 9 cm. in diameter. In taking this and similar photographs reproduced in this paper, the outside surface of the sphere was covered with a layer of dead-black paint except for a horizontal slit, 3 mm. wide, facing the camera. The lens was focussed on a vertical plane passing through the point of ignition at right angles to the axis of the lens, and the sensitised paper can be regarded as moving vertically downwards. There is thus obtained a time–distance graph of the movement of the flame-front across the slit in either direction from the centre to the sides of the sphere. The speed of travel of the paper was recorded by photographing on it the sparks produced at the mercury contacts of an electrically-maintained tuning-fork of 100 frequency. The limits of the vessel are indicated on the photograph by the vertical parallel lines drawn thereon. It will be seen that the flame travelled from the spark at a uniform speed until within 1 cm. of the walls of the vessel, when a gradual retardation began.

It will be convenient to designate these two chief phases in the propagation of flame within a closed vessel, which are exhibited whatever the shape of the vessel, as Phase I and Phase II. During Phase I, which is of far longer duration when the vessel is of large volume, the speed of the flame when ignition is at the centre of a sphere, is nearly uniform. During Phase II the speed gradually decreases.

It will be understood that during Phase I the proper motion of the flame and that of the unburnt mixture ahead of the flame-front have the same direction, the unburnt mixture being moved freely as though it were not enclosed. During Phase II, the direction

of motion of the flame and of the mixture may be opposed and combustion proceeds under an enhanced, and increasing, pressure which the mixture began to experience after Phase I of the propagation of flame had come to an end. Even the most sensitive pressure-gauge, without appreciable "lag," attached to the wall of the vessel, does not begin to register pressure until Phase I of the propagation of flame has ceased. This will be demonstrated in another communication.

We are particularly concerned in the present investigation with the behaviour of the flame during Phase II, and with the condition then obtaining of the products of combustion of Phase I. In our study thereof we have employed mainly the method of "snap-shot" photography previously described (J., 1925, **127**, 764), using carbon monoxide as the inflammable gas.

*Explosions within a Sphere.*—The series of photographs on Plate II was taken at successive stages during the explosion of a mixture of carbon monoxide and air containing 32·35% of carbon monoxide (corresponding almost to $2CO + O_2 + 3N_2$), saturated with water vapour at 15·5°, initially at atmospheric pressure. The explosion-vessel was a glass sphere, 9 cm. in diameter. Ignition was by a single secondary discharge at a 1·5 mm. spark-gap between platinum electrodes at the centre of the sphere. The photographs were taken on a vertical plane through the spark-gap. Each exposure lasted 1·67 millisecs., except that for photograph No. 12, which lasted 3·69 millisecs. For the purpose of reproduction, these photographs have been reduced to one-third of their original size. The boundary of the explosion-vessel is indicated by a white circle drawn on each photograph.

In the mixture used, flame travels at the same speed in all directions from the spark-gap. Its progress in a vertical plane can be traced in the photographs up to and including No. 6, where it can be seen touching the boundary of the vessel simultaneously at all points, the time taken for it to travel from the centre being 13·7 millisecs. It will be observed that the central portion of the vessel has become re-illuminated and remains illuminated long after the flame has touched the walls. The area illuminated gradually decreases, and the luminosity diminishes in intensity but is still appreciable 77·7 millisecs. after ignition or about 64 millisecs. after the flame has reached the boundary.

The point to which we wish to direct particular attention is that the re-illumination at the centre of the vessel began before the flame had touched the walls. It began, in fact, as soon as, or just after, what we have termed Phase II of the propagation began. At this instant, photograph No. 5 shows the presence of (i) a spherical

PLATE I.

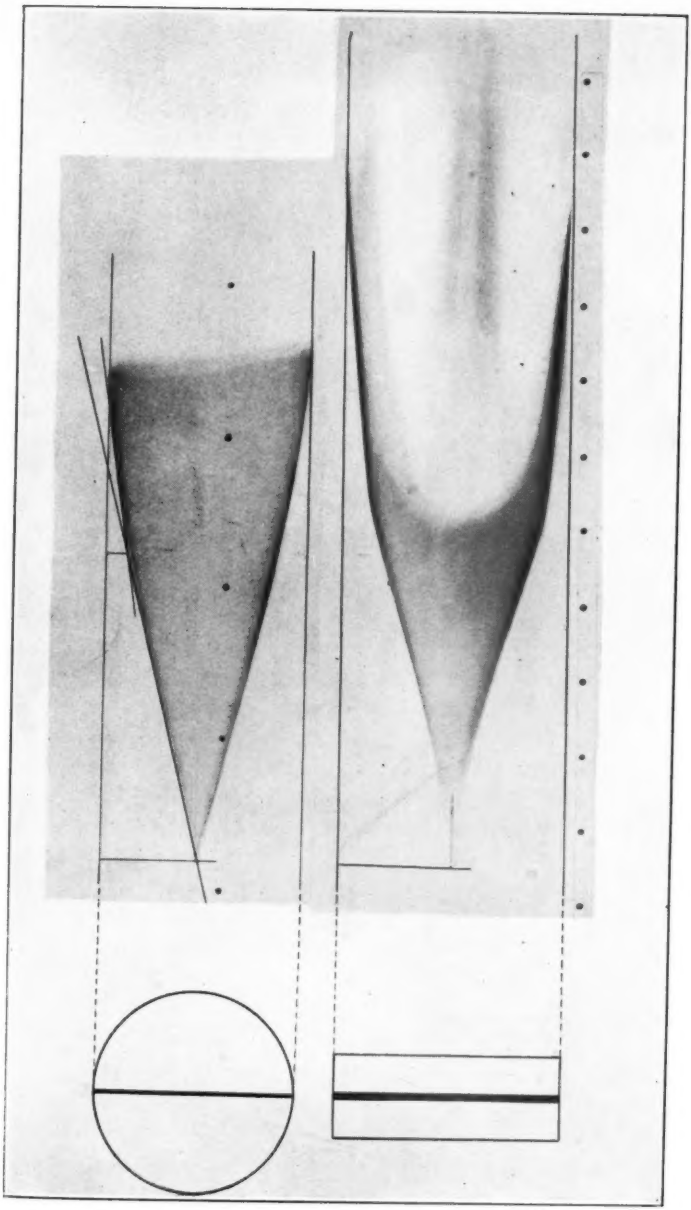
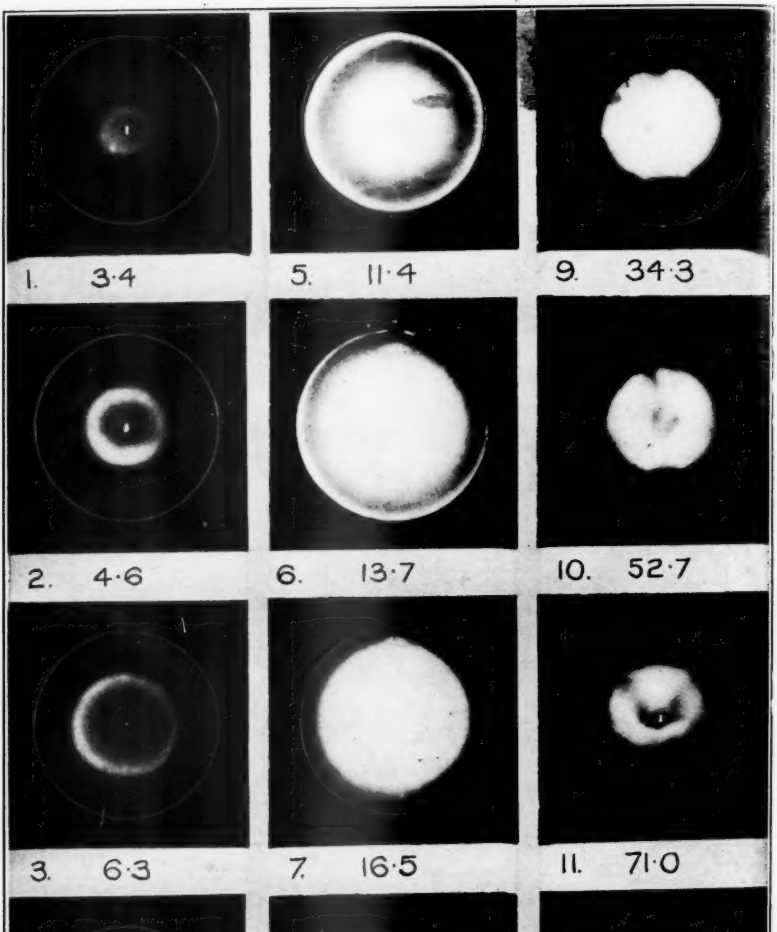


FIG. 1. FIG. 2.

[*To face page* 312.]

PLATE II.




*The figures below each photograph record the times after ignition, in milliseconds, at which the photograph was taken.*

shell of unburnt mixture between the flame-front and the walls of the explosion-vessel (non-luminous); (ii) the flame-front (luminous); (iii) the products of combustion just behind the flame-front (faintly luminous); and (iv) the residual gases from Phase I (brightly luminous).

*Explosions within a Cylinder.*—When the explosion occurs within a cylinder, the two chief phases in the propagation of flame have rather different characteristics from those of the corresponding phases when the explosion-vessel is spherical, but they are perhaps more clearly defined.

The photograph reproduced in Fig. 2 on Plate I was obtained in the same manner as that shown in Fig. 1 and should be compared with it. The explosion-vessel was a horizontal cylinder, 6 cm. in diameter and 16 cm. long. A 21·8% mixture of carbon monoxide and air was ignited at the centre of the vessel. The photograph is a time–distance graph of the movement of the flame-front along the axis of the cylinder in either direction from the centre to the ends. Phase I, during which the speed of the flame-front along the axis of the cylinder accelerates, ends just after the flame-front travelling transversely from the point of ignition has reached the walls of the cylinder. During Phase II the speed of the flame-front, which is now travelling in either direction horizontally only, is considerably retarded. In a cylinder of larger diameter the speed of the flame during Phase I is nearly uniform.

The series of photographs reproduced on Plate III are of stages in the explosion of a 27·7% mixture of carbon monoxide and air in the same cylinder, ignition being at the centre. The mixture was saturated with water vapour at 18° and was initially at atmospheric pressure. The intervals after ignition at which the photographs were taken are recorded below them. Each exposure lasted 2 millisecs.

As in a spherical explosion-vessel, the flame begins to travel at a uniform speed in all directions from the spark-gap, but it soon becomes egg-shaped because of its tendency to travel towards the ends of the cylinder rather than towards the sides. Phase I came to an end in photograph No. 4, 20·5 millisecs. after ignition, and signs of re-illumination at the centre of the vessel are noticeable (in the original negative) in the next photograph, taken 4·1 millisecs. later. The luminosity is well marked in photograph No. 7, just before the flame reaches the ends of the cylinder, and persists during at least 40 millisecs. after the flame has reached the ends, ultimately assuming a distinctive shape.

Similarly, numerous series of experiments, with different explosive mixtures ignited at different points within closed vessels of various

shapes, have all shown that, when the luminescence we have described occurs, its inception corresponds with the beginning of Phase II. When ignition of the mixture is central with respect to the walls of the containing vessel, the luminous zone is near the centre; when ignition is asymmetric, the luminous zone occupies a position nearly central with respect to the contour of the flame-front at the end of Phase I; when there is multiple ignition, there is a luminous zone in the neighbourhood of each point of ignition. The luminescence must therefore be exhibited by the residual gases from Phase I of the propagation of flame.

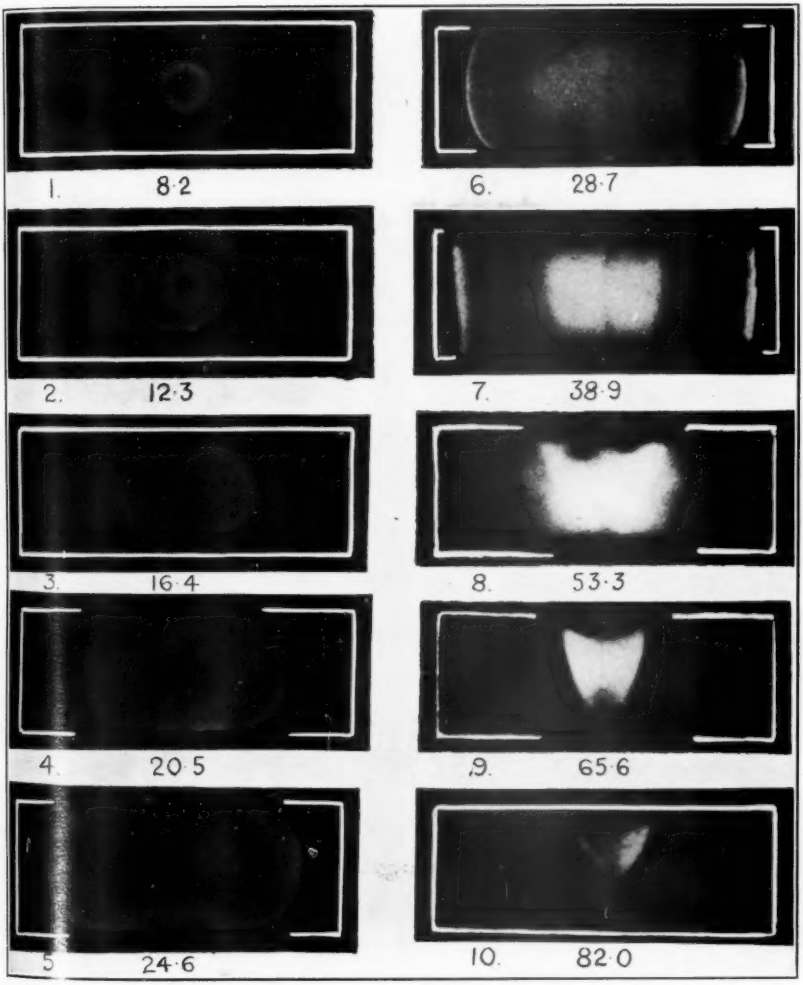
Three possible explanations of this luminescence suggest themselves. It may be due to (i) the re-association of dissociated molecules of carbon dioxide or steam; (ii) the dissociation of such molecules; or (iii) the completion of the combustion of molecules of (in the present instance) carbon monoxide that escaped being burnt whilst the flame was travelling.

*Re-association.* The zone of gas which exhibits the recrudescence of luminosity is that which was burnt during Phase I of the propagation of flame, *i.e.*, whilst combustion was taking place at comparatively low pressure and low initial temperature, for the unburnt mixture ahead of the flame was moving during this phase. Conversely, no luminosity (or, in some instances, which will be referred to later, but a faint luminosity) can be observed in the products of combustion formed during Phase II, which took place at comparatively high pressure and high initial temperature.

Re-association can only take place in the reactions under consideration on a falling temperature gradient, and the mass of gas in which it begins will be at a lower temperature than the remainder. But the residual gases from Phase I, at the time that they begin to show luminosity, cannot be falling in temperature, for they are being compressed owing to the combustion proceeding during Phase II. The luminescence begins long before any material cooling effect is possible. It is not normally displayed by the products of combustion of Phase II, which include those of the layer of mixture near the boundary of the vessel, when they begin to cool.

A reddish-yellow glow can often be observed after the flame in a closed vessel has completely expired. This glow can reasonably be assumed to be due to reassociation. We have not been able to photograph it, but its inception and duration could be studied by means of our apparatus, the camera being replaced by the eye, which is shielded during successively increasing intervals of time in a series of experiments with the same mixture. This dull glow is observed with mixtures which show no signs of luminescence,

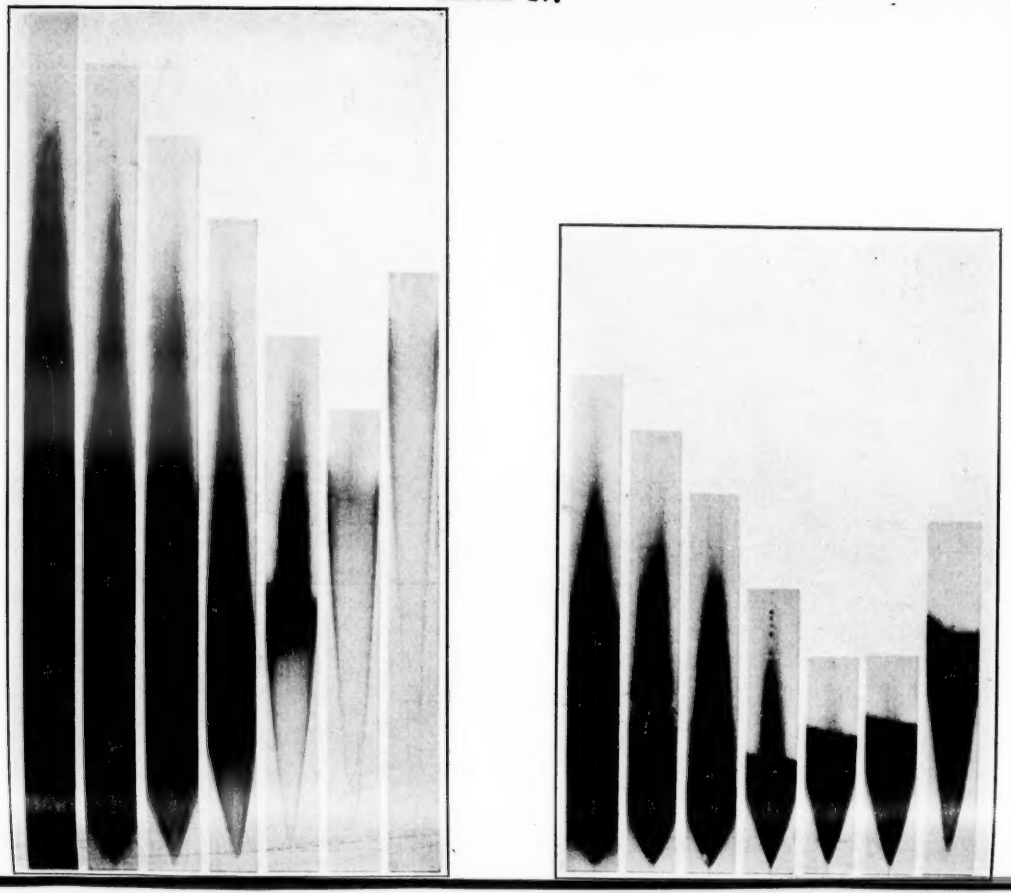
## PLATE III.




*The figures below each photograph record the times after ignition, in milliseconds, at which the photograph was taken.*

[*To face page* 314.]

PLATE IV.



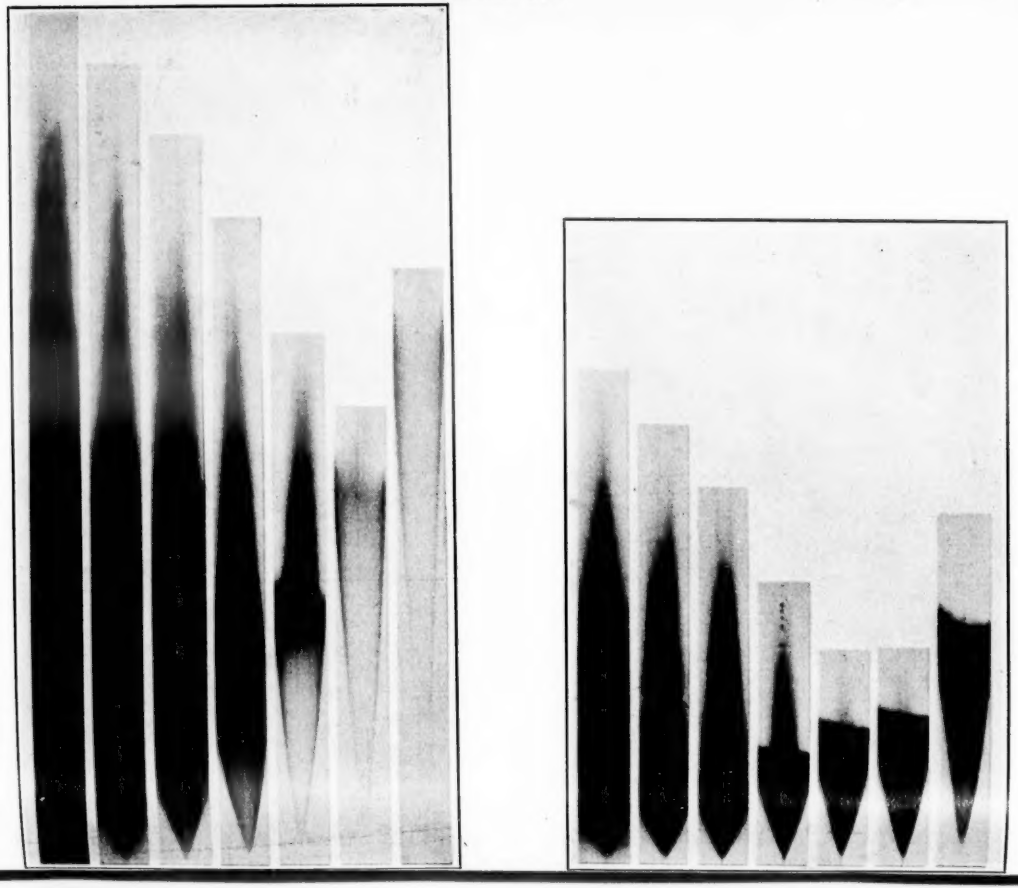
*e.g.*, $2CO + O_2 + 4CO_2$, the calculated flame-temperature of which is about 2230° K., the amount of dissociation of carbon dioxide being about 1·5%. It is quite distinct in character from the luminescence the cause of which we are now considering. This is markedly actinic and leaves an impression on the eye of brilliant whiteness.

*Dissociation.* We have shown that the luminescence begins before material cooling of the gases which exhibit it can have begun. Actually, it would seem that the luminous gases, when they first make their appearance, are at a higher temperature than the products of combustion just behind the flame-front (which is then passing through Phase II) and, after the flame has reached the boundary, they represent the hottest zone within the explosion-vessel (Hopkinson, *Proc. Roy. Soc.*, 1906, *A*, 77, 387). Confirmatory evidence of this is to be seen in the locus of the luminescence within the vessel. In a sphere, when ignition is central, its locus is above the centre of the vessel (Figs. 8—12, Plate II). In a horizontal tube, ignition being at the centre, the central zone of luminescence is banked on both sides, just as banks of warm and cold air occur in the atmosphere, the slant planes heeling over towards the denser medium. This is well illustrated in the last three photographs on Plate III.

The fact that the gases exhibiting the luminescence remain at the highest temperature removes the possibility that dissociation of carbon dioxide or steam is its cause. Such dissociation must be accompanied by the absorption of heat, not by its evolution.

We conclude, then, that the luminescence is due to the completion of the combustion, under increased pressure, of molecules of combustible gas that escaped being burnt whilst the flame was travelling. This is, we believe, the conception of the "after-burning" postulated by Sir Dugald Clerk to account for the "lost" pressure in the gas-engine cylinder when he states: "The explosion is complete when maximum pressure is attained. It does not follow from this that the combustion is complete; that is another matter. The explosion arises from the rapid spreading of the flame throughout the whole mass of the mixture, which may be called the inflammation of the mixture. More or less rapid inflammation means more or less explosive effect, but not complete combustion. The complete burning of the gases present may not occur until long after complete inflammation" (Dugald Clerk, "The Gas, Petrol and Oil Engine," Vol. I, p. 128. London, 1910). We propose to attach this meaning to the term hereafter, despite the fact that it has been used by other writers in a different sense.

PLATE IV.



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*After-burning.*

If after-burning be the true explanation of the luminescence now described, it should be possible to decrease or augment its amount by providing more or less favourable conditions for combustion to take place whilst the flame is travelling.

*The Effect of Concentration of the Reacting Gases.*—A series of mixtures $2CO + O_2 + nO_2$, saturated with water vapour at 0° (*i.e.*, containing 0·63% by volume of water vapour), was fired in a sphere 9 cm. in diameter, ignition being at the centre. Photographic records of the explosions were obtained on a rapidly revolving drum in the manner already described. The secondary discharge that caused ignition was produced in an identical manner in each experiment, the current through the primary circuit of the induction-coil being adjusted to a constant value. The records show (*a*) the total time taken for the flame to travel, in a vertical plane, from the centre to the walls of the vessel, which may be termed the duration of the flame; and (*b*) the duration of the after-burning beyond that of the flame. The results are recorded in Table I.

TABLE I.

*The Explosion of* $2CO + O_2 + nO_2$ *in a Closed Vessel.*

(Mixtures saturated with water vapour at 0°.)

| Value of *n*. | Duration of flame (centisecs.). | Duration of after-burning (centisecs.). |
|---|---|---|
| 2 | 2·7 | 19·7 |
| 3 | 3·3 | 16·9 |
| 4 | 3·75 | 16·25 |
| 5 | 4·9 | 14·7 |
| 6 | 7·7 | 6·4 |
| 7 | 11·3 | 0·8 |
| 8 | 15·1 | Nil. |

The mixture $2CO + O_2 + 9O_2$ is near the lower limit of inflammability. It will be seen that with the mixture $2CO + O_2 + 8O_2$ the concentration of oxygen has enabled the carbon monoxide to be burnt sufficiently completely during Phase I of the propagation to prevent any after-burning outlasting the flame. In each instance the after-burning had its origin in the products of combustion during Phase I of the propagation of flame and began to be noticeable just after Phase II had begun. The products of combustion during Phase II showed no traces of after-burning.

Similarly, in the series $2CO + O_2 + nCO$, saturated with water vapour at 0°, the results recorded in Table II were obtained.

In these mixtures after-burning was evident, from the photographic records, in the products of combustion during Phase II. The photographs of series I and II, reduced in size, are reproduced

TABLE II.

*The Explosion of* $2CO + O_2 + nCO$ *in a Closed Vessel.*

(Mixtures saturated with water vapour at 0°.)

| Value of *n*. | Duration of flame (centisecs.). | Duration of after-burning (centisecs.). |
|---|---|---|
| 4 | 2·1 | 11·2 |
| 5 | 2·3 | 9·3 |
| 6 | 2·5 | 7·8 |
| 7 | 3·4 | 4·7 |
| 8 | 4·2 | 1·8 |
| 9 | 4·4 | 1·5 |
| 10 | 6·9 | Nil. |

on Plate IV. In each photograph, the boundaries of the vessel are at the cut sides of the strip of sensitised paper, and the point of ignition is at the centre of the bottom edge.

In each series of mixtures, the duration of the after-burning clearly corresponds with the speed of propagation of the flame, being greater the greater the speed. For a given speed of flame, the duration of after-burning is less with excess of carbon monoxide than with excess of oxygen, as would be expected from considerations of mass-action. It should be noted that the duration of the after-burning is not necessarily a measure of its amount, although duration and intensity (as judged by the density of the photographic image) appear to be correlated in such series of mixtures as those recorded in Tables I and II.

The amount of gas burnt in accordance with Phase I of the propagation of flame also depends on the speed, for Phase I extends over a greater distance within the vessel the greater the speed. It can be said, therefore, that the amount of after-burning is dependent on the extent to which the propagation of flame takes place in accordance with Phase I.

*The Effect of Water Vapour.*—The duration of after-burning in mixtures of carbon monoxide and air or oxygen decreases rapidly as the amount of moisture present is increased. Now in a given mixture of carbon monoxide and air the presence of water vapour increases the speed of propagation of the "uniform movement" of flame, the optimum quantity being about 6% (W. Shepherd, quoted by Payman and Wheeler, J., 1923, **123**, 1253), and therefore should, according to the experiments just described, allow of greater facility for after-burning. The results for a mixture $2CO + O_2 + 4N_2$ are recorded in Table III.

The mixtures were saturated with water vapour at different temperatures, the initial pressure in each instance being atmospheric. The total mass present grew less, therefore, as the temperature rose, and the proportion of the mixture $2CO + O_2 + 4N_2$

TABLE III.

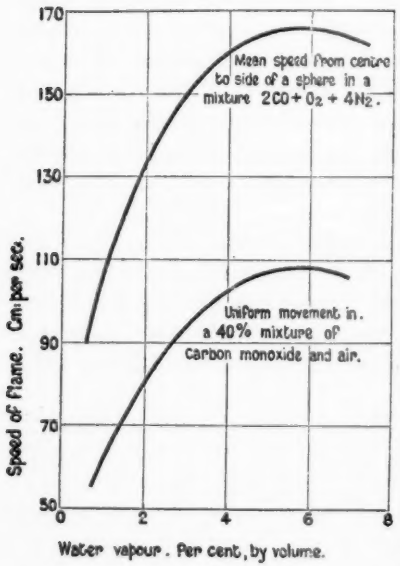
*The Explosion of* $2CO + O_2 + 4N_2$ *in a Closed Vessel.*

(Mixtures saturated with water vapour at different temperatures.)

| Saturation temp. | Water vapour, %. | Duration of flame (centisecs.). | Duration of after-burning (centisecs.). |
|---|---|---|---|
| 0° | 0·63 | 5·1 | 15·8 |
| 5 | 0·85 | 4·7 | 15·1 |
| 10 | 1·21 | 4·0 | 15·2 |
| 15 | 1·68 | 3·6 | 15·0 |
| 20 | 2·31 | 3·2 | 14·1 |
| 25 | 3·13 | 3·0 | 13·7 |
| 30 | 4·20 | 2·8 | 13·2 |
| 35 | 5·55 | 2·7 | 11·6 |
| 40 | 7·28 | 2·8 | 10·4 |
| 45 | 9·47 | 2·8 | 9·7 |

in the mass grew less as the moisture content increased. A graph (Fig. 3) relating percentages of water vapour in the mixture with the mean speed of the flame from the centre to the side of the explosion-vessel bears a close resemblance to that obtained for the uniform movement of flame in a 40% carbon monoxide–air mixture, as determined by Shepherd for a tube 2·5 cm. in diameter (*loc. cit.*), and, as with the uniform movement, shows that the optimum amount of water vapour to develop the full speed of the flame under the conditions of experiment was about 6%.

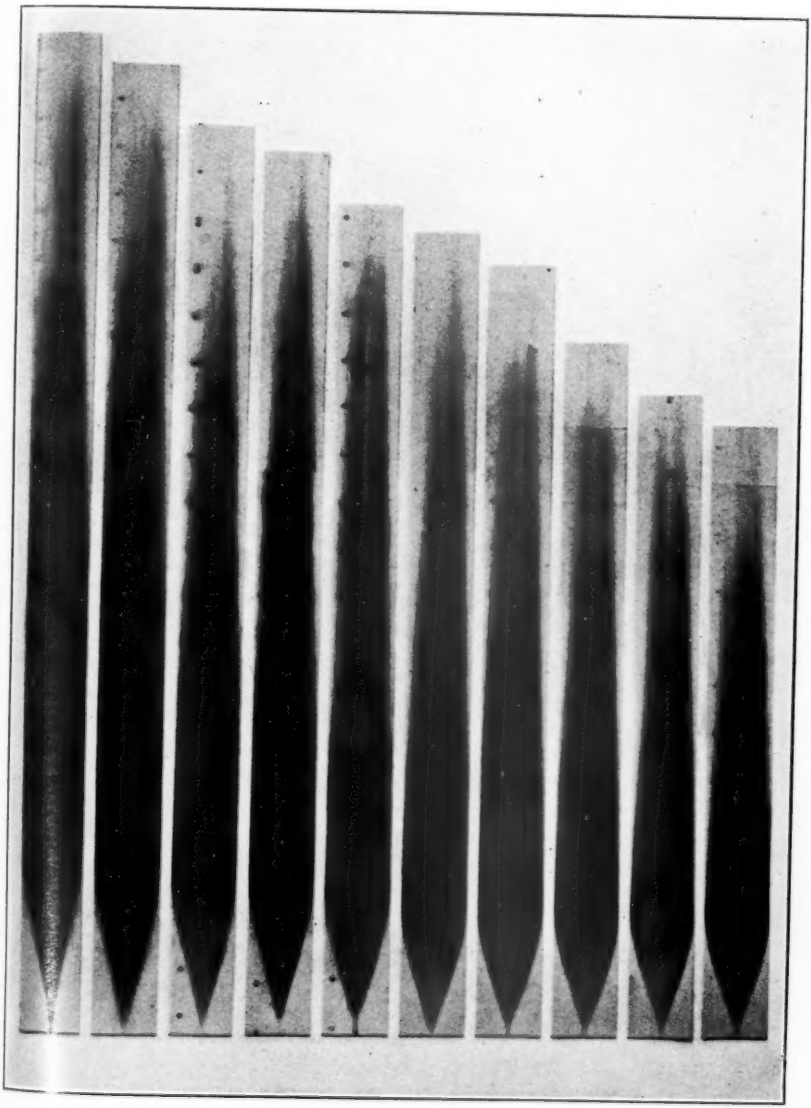
FIG. 3.




The records from which the values recorded in Table III were obtained are reproduced in Plate V. It will be seen that, despite the fact that the mean speed of the flame increased, both the duration and intensity of the luminescence decreased markedly as the moisture-contents of the mixtures increased. This effect we ascribe to the greater ease of combustion of the carbon monoxide during Phase I of the propagation of flame, due to the presence of the water vapour, there being in consequence less residual combustion or "after-burning."

*The Effect of Diluent Gases.*—Series of experiments were made in which different diluent gases, nitrogen, argon, and helium, were

PLATE V.



[*To face page* 318.]

added to the basic mixture $2CO + O_2$ in the same proportions, in order to vary the speed of flame without altering the relative concentrations of the combining gases. In each series, the proportion of water vapour was varied by saturating the mixtures at known temperatures. The results are recorded in Table IV.

TABLE IV.

*The Explosion of* $2CO + O_2 + 4X$ *in a Closed Vessel.*

*Duration of* (a) *Flame and* (b) *After-burning* (*centiseconds*).

| Saturation temp. | Water vapour %. | X = $N_2$. (a). | X = $N_2$. (b). | X = A. (a). | X = A. (b). | X = He. (a). | X = He. (b). |
|---|---|---|---|---|---|---|---|
| 0° | 0·63 | 5·1 | 15·8 | 3·4 | 20·3 | 2·1 | 16·6 |
| 5 | 0·85 | 4·7 | 15·1 | 3·2 | 19·2 | 2·1 | 16·2 |
| 10 | 1·21 | 4·0 | 15·2 | 2·9 | 18·4 | 1·8 | 14·9 |
| 15 | 1·68 | 3·6 | 15·0 | 2·6 | 17·6 | 1·55 | 14·55 |
| 20 | 2·31 | 3·2 | 14·1 | 2·4 | 17·2 | 1·5 | 13·6 |
| 25 | 3·13 | 3·0 | 13·7 | 2·2 | 16·1 | 1·3 | 13·2 |
| 30 | 4·20 | 2·8 | 13·2 | 2·1 | 16·0 | 1·15 | 13·2 |
| 35 | 5·55 | 2·7 | 11·6 | 2·0 | 15·1 | 1·1 | 12·9 |
| 40 | 7·28 | 2·8 | 10·4 | 2·0 | 14·1 | 1·2 | 12·3 |
| 45 | 9·47 | 2·8 | 9·7 | 2·0 | 11·6 | 1·3 | 10·7 |

Similarly, dilution of the basic mixture $2CO + O_2$ was effected by the participants in the equilibrium $2CO + O_2 \rightleftharpoons 2CO_2$, with the results shown in Table V.

TABLE V.

*The Explosion of* $2CO + O_2 + 4Y$ *in a Closed Vessel.*

*Duration of* (a) *Flame and* (b) *After-burning* (*centiseconds*).

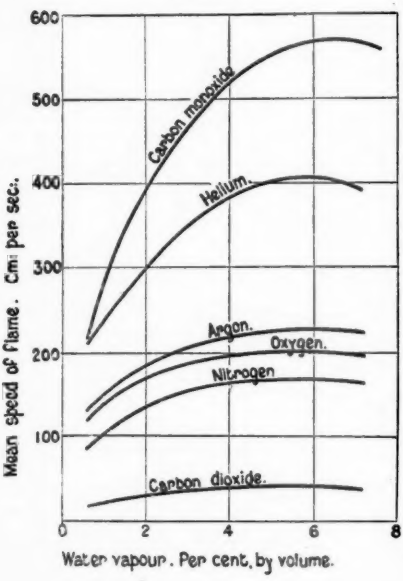
| Saturation temp. | Water vapour %. | Y = CO. (a). | Y = CO. (b). | Y = $O_2$. (a). | Y = $O_2$. (b). | Y = $CO_2$. (a). | Y = $CO_2$. (b). |
|---|---|---|---|---|---|---|---|
| 0° | 0·63 | 2·1 | 11·2 | 3·75 | 16·25 | 23·3 | 11·5 |
| 5 | 0·85 | 1·8 | 11·3 | 3·3 | 16·3 | 20·4 | 11·0 |
| 10 | 1·21 | 1·45 | 10·35 | 3·0 | 16·0 | (Not determined.) | |
| 15 | 1·68 | 1·25 | 9·85 | 2·8 | 15·0 | 15·9 | Nil. |
| 20 | 2·31 | 1·1 | 9·3 | 2·6 | 14·0 | 13·9 | ,, |
| 25 | 3·13 | 0·95 | 9·3 | 2·5 | 13·5 | 12·7 | ,, |
| 30 | 4·20 | 0·85 | 9·15 | 2·4 | 12·8 | 12·5 | ,, |
| 35 | 5·55 | 0·8 | 8·9 | 2·2 | 12·8 | 11·3 | ,, |
| 40 | 7·28 | 0·75 | 7·95 | 2·3 | 11·5 | 11·75 | ,, |
| 45 | 9·47 | 0·8 | 7·4 | 2·3 | 10·5 | 11·8 | ,, |

From these series of experiments, we can form some judgment as to the effects of the various factors that influence the transference of heat during and after the propagation of flame, on flame-speed, and on the duration of after-burning.

The effect on flame-speeds can be studied by means of graphs

(Fig. 4) relating mean speeds of flame (measured from the centre to the side of the explosion-vessel) with percentages of water vapour in the different mixtures. As with the uniform movement of flame (Coward and Hess, quoted by Payman and Wheeler, Faraday Society Discussion, June 14th, 1926), the dependence of the flame-speed on the specific heat of the diluent gas and on its conductivity is readily apparent in the series of mixtures. The most striking comparison lies, however, in the effect of increasing the concentration of water vapour when excess of either of the two reacting gases, carbon monoxide and oxygen, is used as diluent. The effect is much more marked when carbon monoxide is in excess, although, as with all the diluents, the same optimum concentration of water vapour is indicated. The extent to which the reactivity of carbon monoxide is dependent on the presence of water vapour is thus strikingly displayed.

FIG. 4.



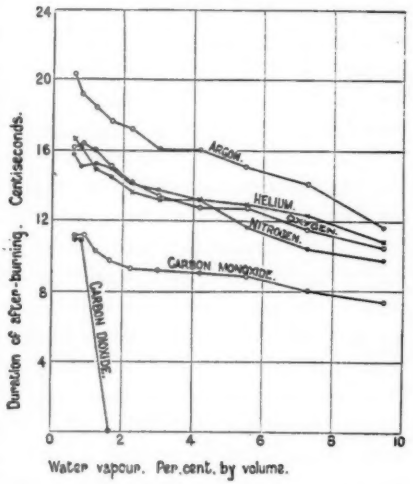

As regards the duration of after-burning, it will be understood that the records given are of the after-burning subsequent to the flame reaching the walls of the explosion-vessel, whereas we have shown that indications of after-burning begin before the flame reaches the walls. It is conceivable, in fact probable, that the inception of after-burning in the series of experiments recorded in Tables IV and V has varied with the character of the diluents X and Y. We cannot, from our present records, form an absolute estimate of the extent of variation in the time of inception of after-burning with the different mixtures (it appears to begin just after Phase II of the propagation begins); but, since by far the greater proportion of the after-burning occurs subsequent to the flame reaching the walls of the explosion-vessel, comparison of the figures recorded in Tables IV and V should serve our purpose.

It can be assumed that the amount of after-burning (residual combustion), as gauged by its duration, might be dependent upon (*a*) the degree of incompleteness of combustion during the propag-

ation of flame, and (*b*) the facility afforded for the residual combustion to proceed. Any factor that would tend to accelerate the residual combustion would shorten its duration, and might increase its intensity.

In the several series of experiments that we have carried out, by progressively increasing the concentration of water vapour up to the optimum for the combustion of carbon monoxide, we have provided, with each diluent gas, a gradually increasing facility for completeness of combustion during the propagation of flame. By studying the general trend of variation in the duration of after-burning throughout each series, we should therefore be able to gauge the relative effect of the presence of each diluent gas in accelerating or retarding the residual combustion, as distinct from its original influence on the completeness of combustion during the propagation of flame. In Fig. 5, the duration of the after-burning, beyond that of the flame, is plotted against the proportion of water vapour in the mixtures for each of the series $2CO + O_2 + 4X$ (or 4Y).

FIG. 5.




All the photographs from which the records in Tables IV and V were obtained were taken on Lumière paper from the same source of supply. They were developed during the course of one day, each being treated during 150 secs. in a bath of standard developer at a uniform temperature of 5°. The duration of after-burning can be measured accurately within 0·1 centisec.

A fact to be noted is that no support can be obtained for the suggestion that the luminescence that we ascribe to after-burning may be due to the recombination of dissociated carbon dioxide or steam molecules. The amount of dissociation would be greatest with those mixtures having the highest "flame-temperature." The duration of after-burning is, for all concentrations of water vapour, greatest with the argon mixtures (calculated flame-temperatures, 3520° K.), and is markedly greater than with the helium mixtures, for which the calculated flame-temperatures are the same. Moreover, the duration of after-burning with the helium mixtures is nearly the same as with the nitrogen and the oxygen mixtures,

although the calculated flame temperatures for these are much lower (2890° K.). With the carbon monoxide mixtures (calculated flame temperatures, 2890° K.), the duration of after-burning is throughout considerably the shortest. With the carbon dioxide mixtures, in which the speed of flame is exceptionally slow (calculated flame-temperatures, 2230° K.), there is no after-burning when the concentration of water vapour exceeds about 1·5%, but with the lowest concentration (0·63%) it is nearly as long as with carbon monoxide.

We are unable at present to offer a complete explanation of the effect of argon. We have noticed that, not only is the duration of the after-burning longest when this gas is the diluent, but its actinic effect, and that of the flame also, is greatest. In another research, in which the propagation of flame in mixtures of hydrogen and air is being studied, the substitution of argon for the nitrogen has been found greatly to affect the actinic power of the flames. It may well be that in these experiments the high actinic value of the luminescence when argon is present enables it to be registered photographically for a longer period than in the other series.

This leads us to a consideration of the relative actinic effects of the luminescence and of the flames. The photographs reproduced on Plates II and III show, what is a general observation, that the luminescence has a greater effect on a photographic plate than the flame itself. It is true that the flame is moving whilst it is being photographed, whereas the luminescence is nearly stationary, but, making allowance for this, the difference is so great as to suggest that different forms of radiation are being emitted during the two phenomena of flame propagation and after-burning. On the other hand, there is no evidence that the chemical reactions during the after-burning differ in character from those during the propagation of flame. On the contrary, it is clear (see Fig. 5) that the combustion of carbon monoxide during the after-burning is facilitated by the presence of water vapour just as it is during the propagation of flame. The actinic power of the luminescence may therefore be due solely to the fact that the combustion of the residual carbon monoxide is proceeding at a high temperature and pressure. This question can perhaps be determined by spectroscopic methods of research, which we now have in hand. The research is being continued, also, to include the combustion of gases other than carbon monoxide.

Our thanks are due to the Safety in Mines Research Board for permission to publish this paper.

SAFETY IN MINES RESEARCH LABORATORIES,
SHEFFIELD. [*Received, September 30th*, 1926.]

# XLIX.—*The Reduction of* o-*Nitrophenyl*iso*diazomethanes.*

By FREDERICK DANIEL CHATTAWAY and ARTHUR JOHN WALKER.

IN previous papers it has been shown (J., 1925, **127**, 1687, 2407) that the direct action of halogens upon the nitrobenzaldehydephenylhydrazones leads to substitution in the ω-position; *e.g.*,

$$C_6H_5\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot NO_2 \xrightarrow{3Br_2} C_6H_3Br_2\cdot NH\cdot N{:}CBr\cdot C_6H_4\cdot NO_2.$$

Of these ω-halogen derivatives, those derived from *o*-nitrobenzaldehydephenylhydrazone behave in an anomalous manner, easily splitting off halogen acid and forming explosive compounds. The α-hydrogen and the ω-halogen atom are eliminated in this change, which is simply accounted for by assuming the formation of a three-atom *iso*diazomethane ring thus:

$$C_6H_3Br_2\cdot NH\diagup\!\!\!\diagdown N\!=\!CBr\cdot C_6H_4\cdot NO_2 \longrightarrow$$

$$HBr + C_6H_3Br_2\cdot N\diagup\!\!\!\diagdown N\!=\!C\cdot C_6H_4\cdot NO_2.$$

A number of these *o*-nitrophenyl halogenophenyl *iso*diazomethanes have been described (*loc. cit.*, p. 2410) and the present paper is concerned with a further study of their properties, and notably of the products they yield on reduction.

They are all well-crystallised, yellow substances which can be kept indefinitely at the ordinary temperature without change but explode with great violence when heated. In hot solution, they suffer decomposition to a greater or less extent. Those containing three halogen atoms in the nucleus are markedly more stable than those with less halogen. They are stable towards acids, and show feebly basic properties, dissolving in concentrated hydrochloric acid, for example, and being reprecipitated on dilution. When hydrogen chloride is passed into their dry ethereal solutions, colourless addition compounds are precipitated. These readily lose hydrogen chloride and revert to the original compounds on exposure to air, or on moistening with water.

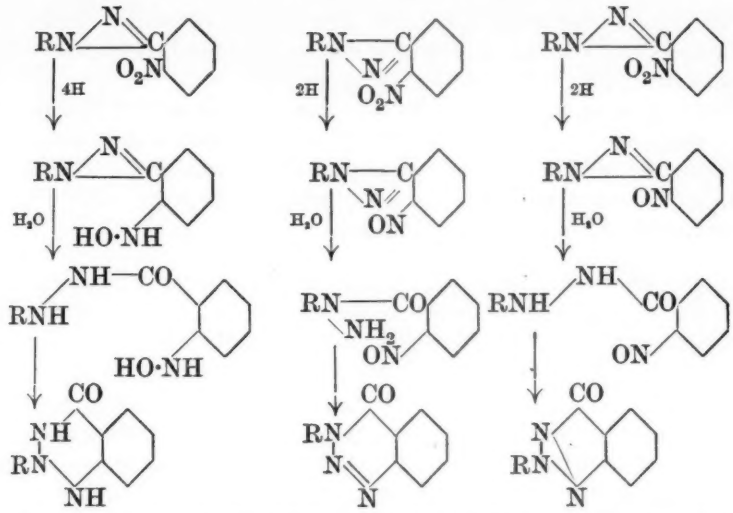
They are all rapidly decomposed by alcoholic potash, or alcoholic ammonia, yielding as one of the products a halogen-substituted benzene (*e.g.*, *o*-nitrophenyl-2 : 4 : 6-trichlorophenyl*iso*diazomethane yields 1 : 3 : 5-trichlorobenzene).

On oxidation with permanganate they yield *o*-nitrobenzoic acid.

*Behaviour on Reduction.*—When the *o*-nitrophenyl halogenophenyl *iso*diazomethanes are boiled for some time with alcohol they undergo reduction to almost colourless compounds, the alcohol being simultaneously oxidised to acetaldehyde. The same reaction can more conveniently be effected by the action of stannous chloride in the cold.

The products are well-crystallised compounds, and their analysis shows that in every case they are formed by loss of one atom of oxygen from the original *iso*diazomethane; *e.g.*,

$$C_6H_2Cl_3\cdot N\!<\!\!\!



(I.) Dibromophenyl-dihydrobenztriazone. (II.) Dibromophenyl-benztriazone. (III.) *cycloazi*-Dibromophenyl-benztriazone.

*The first* of these possibilities is excluded by the fact that the compound in question forms no acetyl derivative, and is unaffected by nitric or nitrous acid. Further, the minimum quantity of stannous chloride required for its production does not correspond with that required by this formula.

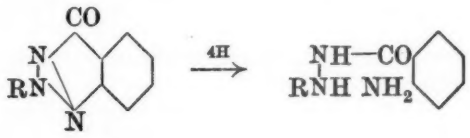
*The second* (II) of these was synthesised directly for comparison, by the method of Mehner (*J. pr. Chem.*, 1901, **63**, 279) from methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate :

$$C_6H_4<\begin{matrix}CO_2Me\\N{:}N{\cdot}NHR\end{matrix} = (II) + MeOH.$$

The product proved *not* to be identical with the reduction product of the *iso*diazomethane, and constitution (II) is therefore excluded.

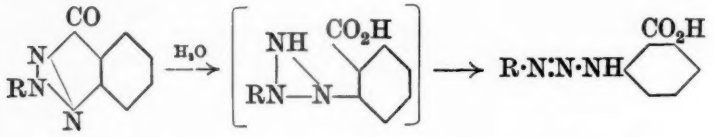
Formula (III) has been adopted, since it accounts in a satisfactory way for the products obtained when the compound is subjected to further reduction, and when it is decomposed by alkalis.

*Reduction.* On reduction in the cold with tin and hydrochloric acid, it yields o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine* :



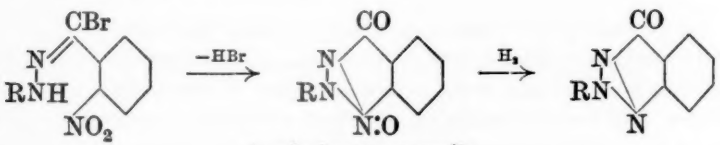
which yields dibromophenylhydrazine and anthranilic acid on hydrolysis and is identical with the compound obtained by reducing *o*-nitrobenzoyl-2 : 4-dibromophenylhydrazine.

*Decomposition by potash.* By the action of alcoholic potash in the cold, the compound yields 2 : 4-*dibromodiazoaminobenzene-2′-carboxylic acid* * identical with the acid obtained by coupling dibromobenzenediazonium chloride with anthranilic acid. The decomposition † may be represented :




The constitution of the reduction product is therefore well established, and there is no doubt that those obtained from similar *iso*diazomethanes are analogously constituted.

The preceding work suggests that an *alternative to the* iso*diazomethane structure* ought to be considered. By assuming an *iso*diazomethane structure for the explosive compounds we have a simple explanation of their formation from the ω-halogen derivatives (see p. 323). On the other hand it has to be borne in mind that the power to form these explosive compounds is limited to those ω-halogen derivatives containing the nitro-group in the ortho-position. This suggests that the reaction may be one in which the nitro-group (by virtue of its ortho-position) actually takes part, and the subsequent reduction to benztriazones lends support to this view. On this alternative theory the explosive compound might be represented as a nitrosoazi-compound, which would naturally pass into the triazone on reduction,

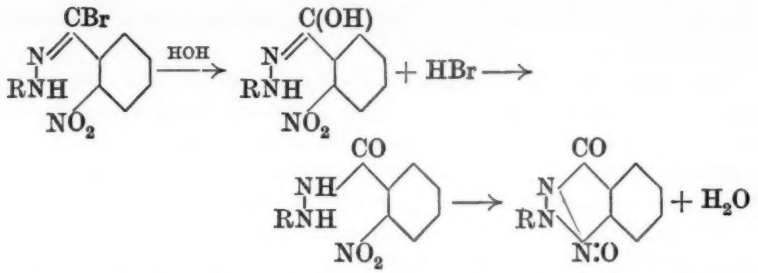



(explosive compound)
(alternative structure)

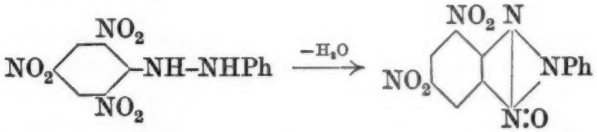
the formation from the ω-halogen derivative taking place by hydrolysis of the halogen, and ring closure involving the nitro-group :

* At the same time, an isomeric acid is produced, which is probably the corresponding aminoazo-compound.

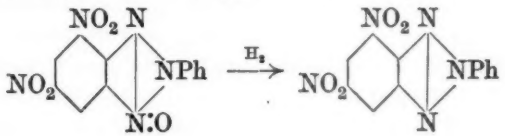
† The highly explosive compound formed when this is carried out in presence of silver nitrate (p. 328) may be a derivative of the intermediate compound (not isolated), written in brackets.



The work of Willgerodt (*J. pr. Chem.*, 1897, **55**, 375; compare also Werner and Stiasny, *Ber.*, 1899, **32**, 3266) on nitrohydrazobenzenes favours this interpretation. He finds that hydrazobenzenes containing a nitro-group in the ortho-position can lose water in the following way,



forming nitrosoazi-derivatives. These, like the explosive compounds here described, are easily reduced (by boiling alcohol) to the corresponding azimido-compounds.



## EXPERIMENTAL.

*Reduction of* 1-2′ : 4′-*Dibromophenyl*-3-o-*nitrophenyliso*diazomethane *to* cycloazi-*Dibromophenylbenztriazone* (III).—(a) *With alcohol.* 2 : 4-Dibromophenyl-*o*-nitrophenyl*iso*diazomethane (5 g.) was boiled under reflux with 100 c.c. of alcohol for 3—4 hours. The solution thus obtained was boiled for another hour, and a few c.c. were then distilled off. These contained acetaldehyde, detected by its smell, and by its action upon Fehling's solution, ammoniacal silver nitrate, and Schiff's reagent. The main bulk of the solution, on cooling, deposited colourless crystals of cycloazi-2 : 4-*dibromophenylbenztriazone*. Recrystallised from alcohol, in which it is moderately easily soluble, it forms long, colourless needles, m. p. 178° (yield, 3 g.) (Found : Br, 42·1. $C_{13}H_7ON_3Br_2$ requires Br, 42·0%).

(b) *With stannous chloride.* For the preparation of larger quantities, this method is more convenient. 2 : 4-Dibromophenyl-*o*-nitrophenyl*iso*diazomethane (10 g.) was ground to a paste with

60—70 c.c. of acetic acid, and 200 c.c. of concentrated hydrochloric acid added.

The whole formed a clear yellow solution, which was maintained at 10—15° while a solution of 15 g. (excess) of stannous chloride in 50 c.c. of concentrated hydrochloric acid was slowly run in with vigorous stirring. The reduction product, which meanwhile separated as a pale yellow precipitate, was washed with dilute hydrochloric acid and then with hot water and finally recrystallised from alcohol; m. p. 178° (yield, 7 g.).

*General properties.* The compound is remarkably stable, and when heated under reduced pressure above its melting point distils with only slight decomposition. It is insoluble in dilute mineral acids, but dissolves in hot concentrated sulphuric, hydrochloric, and nitric acids; from these solutions, it is precipitated unchanged by dilution.

It does not react with nitrous acid, and is recovered unchanged after 8 hours' boiling with acetic anhydride and a drop of sulphuric acid or with acetic anhydride and anhydrous sodium acetate. It is, however, decomposed by alcoholic potash, yielding a deep red solution (see p. 331).

When a solution of the compound in alcohol is warmed with a few drops of ammoniacal silver nitrate solution, and a little caustic potash, a black, amorphous precipitate is slowly formed. If this be touched with a glass rod, or in any way disturbed, under the supernatant liquid, it explodes sharply with great violence, invariably shattering the tube.

*Analogous Reduction Products.*—By the action of boiling alcohol, or of stannous chloride in the cold, other halogenophenyl-*o*-nitrophenyl*iso*diazomethanes yield reduction products, *cycloazi*-phenylbenztriazones, closely resembling the one described. For the sake of the additional analytical data which they afford, three of these were prepared and analysed.

cycloazi-p-*Bromophenylbenztriazone* was prepared from *p*-bromophenyl-*o*-nitrophenyl*iso*diazomethane by both methods. It crystallises from alcohol, in which it is moderately easily soluble, in pale yellow needles, m. p. 197° (Found: Br, 26·4. $C_{13}H_8ON_3Br$ requires Br, 26·5%).

cycloazi-2 : 4-*Dichlorophenylbenztriazone* was prepared from dichlorophenyl-*o*-nitrophenyl*iso*diazomethane by both methods. It exists in two polymorphic forms. The labile form separates from alcoholic solution in compact, yellow prisms, m. p. 167°; these, in contact with the mother-liquor, dissolve and the stable form appears as colourless needles, m. p. 157°. At the ordinary temperature, in contact with a saturated alcoholic solution, the yellow form slowly

changes into the colourless (Found: C, 54·0; H, 2·6; N, 14·3; Cl, 24·2; *M*, in phenol, 272. $C_{13}H_7ON_3Cl_2$ requires C, 53·9; H, 2·5; N, 14·4; Cl, 24·3%; *M*, 292).

cycloazi-2 : 4 : 6-*Trichlorophenylbenztriazone* prepared from 2 : 4 : 6-trichlorophenyl-*o*-nitrophenyl*iso*diazomethane by both methods, crystallises from alcohol, in which it is only moderately readily soluble, in colourless needles, m. p. 258° (Found: C, 47·7; H, 2·1; N, 13·5; Cl, 32·4; *M*, in phenol, 300. $C_{13}H_6ON_3Cl_3$ requires C, 47·8; H, 1·9; N, 12·85; Cl, 32·6%; *M*, 326·5).

*Synthesis of Isomeric Phenylbenztriazones for Comparison.*—p-*Bromophenylbenztriazone* (II; R = *p*-$C_6H_4Br$). A solution of 3 g. (1 mol.) of methyl anthranilate in 5 c.c. (2·5 mols.) of concentrated hydrochloric acid and 30 c.c. of water was diazotised at 0° with 1·4 g. (1 mol.) of sodium nitrite. A solution of 3 g. of *p*-bromoaniline in dilute hydrochloric acid was added, and then excess of a cold solution of sodium acetate; methyl *p*-bromodiazoaminobenzene-*o'*-carboxylate slowly separated. It crystallised from alcohol, in which it is moderately easily soluble, in golden-yellow needles (yield, 4·5 g.), m. p. 120° (Found: Br, 24·9. Calc.: Br, 24·8%).

The conversion into p-*bromophenylbenztriazone* was effected by boiling for 2 hours with a mixture of 2 vols. of alcohol and 1 vol. of water; on cooling, the benztriazone separated in colourless crystals.

Recrystallised from alcohol, in which it is moderately easily soluble, it separated in colourless plates, m. p. 196°, which proved quite distinct in appearance and properties from the reduction product of *p*-bromophenyl-*o*-nitrophenyl*iso*diazomethane, m. p. 197°. A mixture of the two melted below 190° (Found: Br, 26·5. $C_{13}H_8ON_3Br$ requires Br, 26·5%).

2 : 4-*Dibromophenylbenztriazone* (II). Attempts to obtain methyl 2 : 4-dibromodiazoaminobenzene-2'-carboxylate from methyl anthranilate and dibromoaniline by diazotising and coupling in the usual way were unsuccessful, as the addition of sodium acetate to the acid solution of diazonium salt and amine simply reprecipitated the amine (dibromoaniline or methyl anthranilate) unchanged.

This difficulty was overcome by employing acetic acid as solvent in the place of water: To 5 g. (1 mol.) of dibromoaniline, dissolved in 50 c.c. of acetic acid, were added 10 c.c. (5 mols.) of concentrated hydrochloric acid and the mixture was cooled to 0° and diazotised by adding a saturated aqueous solution of 1·4 g. (1 mol.) of sodium nitrite. The diazo-solution was then mixed with a cold solution of 3 g. (1 mol.) of methyl anthranilate in 20 c.c. of acetic acid and 5 c.c. of water. On adding an excess of anhydrous

sodium acetate, the diazoamino-compound slowly separated. After ½ hour, the mixture was diluted considerably with water, and the methyl 2 : 4-dibromodiazoaminobenzene-2′-carboxylate was filtered off and recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in bright yellow needles, m. p. 141° (Found: Br, 40·0. Calc.: Br, 39·9%).

The ester (1 g.) was heated at 100° for 2 hours in a sealed tube with 50 c.c. of alcohol and 10 c.c. of water (Mehner, *J. pr. Chem.*, 1901, **63**, 241). The *triazone* separated as a colourless solid when the cooled product was poured into water. It was crystallised from alcohol, in which it is moderately easily soluble, and from which it separates in compact prisms, m. p. 136° (Found: Br, 42·1. $C_{13}H_7ON_3Br_2$ requires Br, 42·0%).

The compound is quite distinct in appearance and properties from the reduction product of dibromophenyl-*o*-nitrophenyl*iso*diazomethane, m. p. 178° (see p. 327). On boiling for an hour with alcoholic potash it yielded, as the sole product of hydrolysis, 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid, m. p. 151° (see p. 332).

*Reduction of* cycloazi-2 : 4-*Dibromophenylbenztriazone to* o-*Aminobenzoyl*-2 : 4-*dibromophenylhydrazine.*—A solution of 5 g. of *cycloazi*-2 : 4-dibromophenylbenztriazone in 50 c.c. of boiling acetic acid was rapidly cooled with the addition of 40 c.c. of concentrated hydrochloric acid, so that a fine crystalline suspension was obtained. A considerable excess of granulated tin was added, and the whole kept at the ordinary temperature for 5 hours; the original solid had then completely dissolved. The solution was decanted from the tin, diluted with an equal volume of water, and extracted four times with 150—200 c.c. of ether. The ethereal layer was washed with water and dilute sodium carbonate solution, dried over potassium carbonate, and the ether distilled off. The colourless product, o-*aminobenzoyl*-2 : 4-*dibromophenylhydrazine*, exists in two polymorphic forms; when crystallised from alcohol, in which it is moderately easily soluble, it separates first in colourless needles, which in the solvent slowly transform to compact plates; both forms melt at 184°. Yield, 2 g. (Found: Br, 41·55; N, 11·2. $C_{13}H_{11}ON_3Br_2$ requires Br, 41·6; N, 10·9%).

The constitution of *o*-aminobenzoyl-2 : 4-dibromophenylhydrazine was determined by its hydrolysis to anthranilic acid and 2 : 4-dibromophenylhydrazine, and by its synthesis from *o*-nitrobenzoyl-2 : 4-dibromophenylhydrazine by reduction.

*Hydrolysis.* The substance, heated with concentrated hydrochloric acid in a sealed tube for 2 hours at 100°, yielded anthranilic acid, m. p. 144°, and 2 : 4-dibromophenylhydrazine; the latter was

identified by conversion into its characteristic, bright red *o*-nitrobenzaldehydehydrazone, m. p. 205°.

*Synthesis.* β-o-*Nitrobenzoyl*-2 : 4-*dibromophenylhydrazine*, prepared by the Schotten-Baumann method from *o*-nitrobenzoyl chloride and dibromophenylhydrazine, crystallised from alcohol, in which it is moderately easily soluble, in yellow needles, m. p. 180° (Found : Br, 38·5. $C_{13}H_9O_3N_3Br_2$ requires Br, 38·55%).

The reduction of this compound with tin in a cold mixture of acetic and hydrochloric acids yielded the same product, *o*-aminobenzoyl-2 : 4-dibromophenylhydrazine, as the reduction of *cycloazi*-dibromophenylbenztriazone, melting at 184° and crystallising in the same two polymorphic forms.

This identity was further established by the preparation and comparison of its mono- and di-acetyl derivatives. o-*Acetamidobenzoyl*-2 : 4-*dibromophenylhydrazine*, $C_6H_3Br_2{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NHAc$, prepared by the action of acetic anhydride alone upon *o*-aminobenzoyldibromophenylhydrazine in the cold, forms colourless needles, m. p. 210° (Found : Br, 37·3. $C_{15}H_{13}O_2N_3Br_2$ requires Br, 37·5%).

o-*Acetamidobenzoyl*-α-*acetyl*-2 : 4-*dibromophenylhydrazine*,

$$C_6H_3Br_2{\cdot}NAc{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}NHAc,$$

prepared by boiling *o*-aminobenzoyldibromophenylhydrazine with acetic anhydride and a drop of sulphuric acid, crystallises from alcohol, in which it is much more soluble than the monoacetyl derivative, in clusters of colourless needles, m. p. 184° (Found : Br, 34·2. $C_{17}H_{15}O_3N_3Br_2$ requires Br, 34·1%).

*The Action of Potash on* cycloazi-2 : 4-*Dibromophenylbenztriazone*. —A solution of 10 g. of *cycloazi*-dibromophenylbenztriazone in 150 c.c. of boiling alcohol was chilled to produce a fine crystalline pulp. A solution of 20 g. of caustic potash in 100 c.c. of alcohol and 5 c.c. of water was then added, and the whole kept at the ordinary temperature for 5—6 hours; the original crystals had then completely dissolved to give a deep red solution.

This solution contains the yellow potassium salt of 2 : 4-dibromodiazoaminobenzene-2′-carboxylic acid, and in addition, smaller quantities of the deep red potassium salt of another, more stable acid, of the same composition. The sparing solubility in aqueous alcohol of the former renders its isolation a comparatively easy matter.

To the red alcoholic solution was added a little more than its own volume of water; the potassium salt of dibromodiazoaminobenzene-2′-carboxylic acid then separated in an impure condition. It was redissolved in a small quantity of alcohol and again precipitated with an equal volume of water (yield, 2—3 g.). It may

be recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in long, slender, pale yellow needles, m. p. 230—240° (decomp.). It is very sparingly soluble in water.

The free 2 : 4-*dibromodiazoaminobenzene-2′-carboxylic acid*, prepared from the potassium salt by treatment with acetic acid, was recrystallised from alcohol, in which it is moderately easily soluble, and from which it separates in yellow needles which melt at 151°, decomposing with a sharp puff. The crystallisations were effected as rapidly as possible, as the substance easily decomposes on prolonged boiling (Found: C, 39·5; H, 3·4; N, 10·1; Br, 40·1. $C_{13}H_9O_2N_3Br_2$ requires C, 39·1; H, 3·9; N, 10·5; Br, 40·2%).

On reduction with zinc in acetic acid, it yielded anthranilic acid and 2 : 4-dibromoaniline. Its constitution was further confirmed by its synthesis direct from anthranilic acid and 2 : 4-dibromobenzenediazonium chloride. The coupling was effected without difficulty in aqueous solution, and the insoluble diazoaminocompound, after recrystallisation from alcohol, melted at 151° and proved to be identical with the compound obtained from *cycloazi*-dibromophenylbenztriazone.

*The Isomeric Acid*, $C_{13}H_9O_2N_3Br_2$.—The red mother-liquors remaining from the precipitation of potassium dibromodiazoaminobenzene-2′-carboxylate (see p. 331) were acidified with acetic acid, whereby a mixture of the free isomeric acids was precipitated as a brownish-red solid. This was separated, and the more easily soluble dibromodiazoaminobenzene-2′-carboxylic acid extracted with 100 c.c. of boiling alcohol. The sparingly soluble residue was crystallised from acetic acid, in which it is sparingly soluble, and separated in orange-red needles (yield, 1 g.), m. p. 275° (Found: C, 39·2; H, 3·7; Br, 40·1%).

The constitution of this acid has not yet been definitely settled, but its properties suggest that it is an aminoazo-derivative. Heated above its melting point, it sublimes in fine red needles. It is feebly basic, forming a colourless hydrochloride, whilst on boiling with acetic anhydride it yields an acetyl derivative, which crystallises from alcohol in yellow needles, m. p. 220°.

Its potassium salt dissolves in alcohol easily, and in water sparingly, forming deep red solutions. A small quantity boiled with zinc dust in acetic acid yielded 2 : 4-dibromoaniline.

*The Action of Potash on* cycloazi-2 : 4-*Dichlorophenylbenztriazone.*—The action of alcoholic potash on *cycloazi*-dichlorophenylbenztriazone is precisely similar to its action on the corresponding dibromo-derivative already described, and yields dichlorodiazoaminobenzene-2′-carboxylic acid, together with another more

stable and deeply coloured acid of the same composition. These acids were separated in the manner described for the dibromo-derivatives.

2 : 4-*Dichlorodiazoaminobenzene-2'-carboxylic acid*, $C_6H_3Cl_2 \cdot NH \cdot N{:}N \cdot C_6H_4 \cdot CO_2H$, prepared from *cycloazi*-dichlorophenylbenztriazone by the action of potash and also directly from dichlorobenzenediazonium chloride and anthranilic acid, crystallises from alcohol, in which it is moderately easily soluble, in yellow needles, which melt at 163—167°, decomposing with a sudden puff (Found: Cl, 23·15; C, 50·2; H, 3·2; N, 13·2. $C_{13}H_9O_2N_3Cl_2$ requires Cl, 22·9; C, 50·3; H, 2·9; N, 13·5%).

On vigorous reduction with zinc in boiling acetic acid, the compound yielded 2 : 4-dichloroaniline, and anthranilic acid, m. p. 144°.

The potassium salt of this acid is almost insoluble in water, and moderately soluble in alcohol, crystallising from the latter in fine, pale yellow needles, m. p. 220° (decomp.).

*The isomeric acid*, $C_{13}H_9O_2N_3Cl_2$, separates from acetic acid, in which it is only sparingly soluble, in orange-red needles, m. p. 275° (Found: Cl, 23·0; N, 13·7%). In its properties it corresponds closely with the very stable, orange-red (dibromo) acid already described, m. p. 275° (see p. 332), subliming above its melting point in fine red crystals. Its potassium salt is sparingly soluble in water, but easily soluble in alcohol, giving a deep red solution.

THE QUEEN'S COLLEGE, OXFORD. [*Received, November 26th*, 1926.]

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## L.—*Contribution to the Physical Chemistry of Complex Salts. Part I. Transport Numbers of Copper Salicylate.*

By WILLIAM EDWARD HAMER and CHARLES R. BURY.

DURING the course of work on the derivatives of copper salicylate [$Cu(HSal)_2$, where $H_2Sal$ = salicylic acid] it seemed desirable to determine its transport number in aqueous solution, with the object of throwing some light on its constitution, for on Werner's theory, the constitution of a complex salt is primarily an expression of its mode of ionisation.

Since hydrogen sulphide readily precipitates copper sulphide from an acid solution * of the salicylate, the latter presumably

* If hydrogen sulphide is passed into a neutral solution of the compound containing no other electrolyte, a colloidal solution of copper sulphide is obtained, just as in the well-known method of preparing mercuric sulphide sols from mercuric cyanide.

dissociates, to some extent at any rate, as a normal salt with formation of copper and salicylate ions. On the other hand, addition of alkali causes only very slow and partial precipitation of copper hydroxide; from these alkaline solutions, compounds of the type $M_2CuSal_2$ (M = Na,K, or $NH_4$) can be isolated (Ley and Erler, *Z. anorg. Chem.*, 1908, **56**, 404), and transport-number determinations—qualitative only, owing to the slow decomposition of the compound—show that copper is here part of the negative ion. Since salicylic acid contains the well-known chelate group, $-C(OH)=C-C=O$, which is characteristic of a number of important complex-forming molecules (*e.g.*, acetylacetone), it is probable that the constitution of these compounds is represented by the formula

$$M_2\left[C_6H_4<\begin{matrix}CO_2\\O\end{matrix}>Cu<\begin{matrix}CO_2\\O\end{matrix}>C_6H_4\right]$$

(Weinland, "Komplex-verbindungen," 1919, p. 193) and that copper salicylate itself is present in solution largely as the corresponding acid, $H_2(CuSal_2)$.

Titration with alkali, the end-point being determined by means of the conductivity (since the deep colour of the solutions prohibits the use of indicators), gave sharply defined V-shaped curves indicating that the compound is a monobasic acid. The evidence is thus in favour of copper salicylate being a complex acid; the precipitation of copper sulphide by hydrogen sulphide merely proves the existence of traces of copper ions in solution.

## Experimental.

Copper salicylate was prepared from copper sulphate and sodium salicylate, washed, recrystallised from water until free from sulphate, and air-dried. Temperatures above 60° were avoided on account of the ready decomposition.

Preliminary experiments showed that the solubility of copper salicylate at 25° is 10·19 g. (0·0302 g.-mol.) per litre of solution: transport-number determinations are thus restricted to somewhat dilute solutions and the highest accuracy is unattainable.

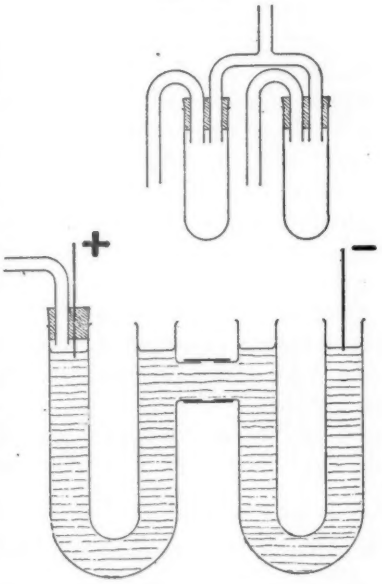
The cell (Fig. 1), of 160 c.c. capacity, constructed throughout from tubing of the same diameter, was made in two pieces and connected by rubber tubing. It was kept in a thermostat at 25·0° ± 0·2°. A current of 10—15 milliamps. was passed between the two platinum electrodes for 1—3 hours; a precipitate (which appears to be the compound CuSal, salicylic acid acting as a dibasic acid) separated at the cathode, causing a rapid increase in the resistance with consequent fall of current; to obviate this, the cathode was lowered slightly every 10 minutes, thus exposing a fresh surface to the

solution. This precipitate caused a stirring of the cathode liquid and also precluded its analysis; the transport numbers are therefore based on analysis of the anode portions only.

During preliminary experiments, inconsistent results were obtained owing to leakage of electricity through the rubber joint into the bath. To eliminate, or alternatively to detect, this source of error, the joint was waxed and two copper voltameters were used, one connected to the anode and the other to the cathode.

At the end of the experiment, two centre portions—the anode centre and the cathode centre portions, each of about 20 c.c.—were withdrawn simultaneously from the two inner limbs by means of the device shown in the upper part of Fig. 1. Withdrawal of the centre portions left the anode and cathode portions isolated in the two U-tubes. The cell was then disconnected at the rubber joint, and the anode portion removed for analysis. All analyses were by weight, not volume of solution. Copper was estimated by Volhard's method (Classen, "Ausgewählte Methoden der Analytischen Chemie," 1901, I, p. 87), since the electrolytic and iodine–thiosulphate methods fail in the presence of salicylic acid.

FIG. 1.




The results are in Table I: cols. 1, 2, and 3 give, respectively, the initial concentrations and the concentrations of the anode-centre

TABLE I.

| Concentrations. | | | Voltameter. | | Anode portion. | | |
|---|---|---|---|---|---|---|---|
| Initial. | Anode-centre. | Cathode-centre. | Anode (g.). | Cathode (g.). | Weight (g.). | Copper (g.). | Transport number of cation. |
| 0·02746 | 0·02755 | 0·02672 | 0·0510 | 0·0508 | 55·83 | 0·06484 | 0·628 |
| | 0·02750 | 0·02701 | 0·0532 | 0·0528 | 52·56 | 0·05766 | 0·633 |
| | 0·02732 | 0·02707 | 0·0406 | 0·0410 | 52·06 | 0·06386 | 0·646 |
| 0·01823 | 0·01816 | 0·01852 | 0·0341 | 0·0341 | 54·89 | 0·04191 | 0·630 |
| | 0·01834 | 0·01849 | 0·0342 | 0·0347 | 58·88 | 0·04621 | 0·627 |
| 0·01399 | 0·01399 | 0·01391 | 0·0214 | 0·0216 | 55·03 | 0·03562 | 0·613 |
| 0·01249 | 0·01247 | 0·01241 | 0·0185 | 0·0187 | 53·24 | 0·03067 | 0·617 |
| | 0·01243 | 0·01250 | 0·0154 | 0·0154 | 53·10 | 0·03244 | 0·623 |
| | | | | | | Mean | 0·626 |

and the cathode-centre portions, in mols. per 1000 g. of water; cols. 4 and 5 show the increase in weight of the cathodes of the two copper voltameters; in cols. 6 and 7 are the weights and copper contents of the anode portion removed after the experiment, and in col. 8 are the calculated values of the transport number of the cation. No change of transport number with concentration can be detected; deviations from the mean appear to be due entirely to experimental error.

*Discussion.*

Neither the mobility of the copper nor that of the salicylate ion is known accurately at 25°, but assuming these to be 54 and 36, respectively, the transport number of the cation of copper salicylate should be 0·60 if it ionised as a normal cupric salt; whereas, if copper salicylate were a complex acid, there should be an increase in concentration of copper at the anode. The agreement of experiment with the first hypothesis, and the fact that the transport number does not change with concentration, show that copper salicylate ionises in aqueous solution as a normal salt—an unexpected result in view of the arguments put forward in the introduction.

Further consideration shows that hydrogen-ion concentration must have a considerable effect on the stability of the complex ion, and that the indisputable evidence for copper salicylate being a complex acid applies only to alkaline solutions. Assuming the existence of the complex negative ion $(CuSal_2)''$, this must dissociate to some extent into its components:

$$2H^{\cdot} + (CuSal_2)'' \rightleftharpoons Cu^{\cdot\cdot} + 2HSal'.$$

For the conditions of equilibrium of this reaction

$$[H^{\cdot}]^2[(CuSal_2)'']/[Cu^{\cdot\cdot}][HSal']^2 = K_s$$
$$\text{or } [(CuSal_2)'']/[Cu^{\cdot\cdot}] = K_s[HSal']^2/[H^{\cdot}]^2$$

where square brackets indicate concentrations, or, more correctly, activities, which at great dilutions are approximately equal to concentrations. The quantity on the left of the second equation is a measure of the stability of the complex ion; if all the copper is present in the form of a complex ion, its value is infinite; if all is present as simple ions, its value is zero. On combining this with the relation $[HSal'][H^{\cdot}] = K_d[H_2Sal]$, where $K_d$ represents the first ionisation constant of salicylic acid, and with the assumption of equality of positive and negative ions, one obtains the equation:

$$\frac{[(CuSal_2)'']}{[Cu^{\cdot\cdot}]} = \frac{K_sK_d^2(2x - [H^{\cdot}])^2}{[H^{\cdot}]^2(2[H^{\cdot}] + K_d)^2} = \frac{4K_sx^2}{[H^{\cdot}]^2} \text{ (approximately)}$$

where $x$ is the total concentration of copper salicylate in solution, independently of its nature. In neutral and alkaline solution, where $[H^{\cdot}]$ is not greater than $10^{-7}$, no error will be caused by using the simpler approximate expression. The stability of the complex ion depends, therefore, on the total concentration of the compound and on the hydrogen-ion concentration; it should be increased about $10^{12}$ fold on passing from neutral to $N/10$-alkaline solution.*

It is possible to make a rough estimate of the value of $K_s$, for in a solution in which the concentration of copper salicylate is $0{\cdot}02M$ and that of sodium hydroxide is $0{\cdot}1N$, copper hydroxide is only precipitated very slowly, which shows that practically all the copper is in the form of complex ion and that the solubility product of copper hydroxide is only just exceeded. Assuming a value of $2 \times 10^{-13}$ for the solubility product (Immerwahr, *Z. anorg. Chem.*, 1900, **24**, 269), $K_s$ is $6 \times 10^{-15}$; in a neutral solution of the same strength (*i.e.*, $0{\cdot}02M$) only one-thousandth of the copper should be present as complex ion. Copper salicylate must therefore undergo a complete change in constitution on passing from neutral to alkaline solution; in other words, it is a "pseudo-acid." The change in colour of its solutions from light blue to dark green, on titration with alkali, will be regarded by many as confirmation of this view.

Similar considerations as to the influence of hydrogen-ion concentration on stability must apply to all complex ions of the type $(MX_n)$, where M is a metal and HX a weak acid, although the equation connecting these factors will depend on the particular complex ion under consideration. It is noticeable that, whilst there are numerous salts containing complex negative ions of this type, the corresponding acids are seldom known; even when they can be prepared, which is only possible with the most stable complex ions, they are unstable compounds.

According to the equation given above, the stability of the complex ion depends on the concentration of the salt; copper salicylate is too insoluble to permit of a study of its transport number over any wide range of concentrations. Preliminary experiments with the very similar, but more soluble, nickel compound, which it is hoped to publish soon, indicate that it resembles the copper compound in dilute solution, and that appreciable quantities of complex ion are present in more concentrated solutions.

It appears to be a corollary of the complete ionisation theory of

* $[H^{\cdot}]$ cannot be varied at will without the addition of acid or alkali; if the presence of this is taken into account, solution of six simultaneous equations leads to a more complicated expression, which reduces to the same approximate form when $[H^{\cdot}]$ is small.

Milner, and of Debye and Hückel, that the terms "pseudo-acid" and "weak acid" are synonymous; it is therefore reasonable to ascribe the behaviour of copper salicylate on titration to the fact that the complex acid, $H_2(CuSal_2)$, is a weak one. With weak dibasic organic acids, the conducto-titrimetric method gives an end-point corresponding to neutralisation of the first hydrogen ion, whilst the second end-point, corresponding to complete neutralisation, is seldom obvious.

*Summary.*

The transport numbers of copper salicylate in aqueous solution have been determined.

Evidence is presented in favour of the view that copper salicylate is a pseudo-acid, and that, whilst in neutral solution it ionises as a normal copper salt, in alkaline solutions it is present as the salt of a complex cuprisalicylic acid.

A consideration of the ionic equilibria involved indicates that the stability of all complex ions of this type depends to a large extent on the concentration of the hydrogen ions in the solution.

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## LI.—*The Ratio of the Heats of Combustion of Benzoic Acid and Salicylic Acid. (A Reply to P. E. Verkade and J. Coops.)*

By ENDRE BERNER.

RECENTLY Verkade and Coops (J., 1926, 1437), in a reply to me (J., 1925, 127, 2747), held that their previously determined value of the heat of combustion of salicylic acid, 5241·7 $cal._{15°}$ per g. (air) (*Rec. trav. chim.*, 1924, **43**, 561), is correct, as new determinations have given the same result. They conclude from this that my value for this heat of combustion, 5237·4 $cal._{15°}$ per g. (air), is too low and that the reason for this might be an error in the heat capacity of my calorimeter. In support of the correctness of their value, they refer to the results of Roth and of Swientoslawski, who found very nearly the same value, *viz.*, 5241·3 and 5242·4, respectively. Notwithstanding this, I am obliged to consider my value of the heat of combustion of salicylic acid to be the correct one, especially as a new comparison of the heat of combustion of a fresh standard sample of benzoic acid, from the Bureau of Standards, with that of purified salicylic acid gave very nearly the same ratio

of the heats of combustion of the two substances, *viz.*, 1·2074 (vac.), as that found previously [1·2073 (vac.)]. In this comparison, as will be seen below, the heat capacity of the calorimeter was not introduced at all into the calculation of the result, the ratio being calculated directly from the rise in temperature when the two substances were burned.

In my previous paper, I was of the opinion that the difference between my value and that of Verkade and Coops was due to insufficient purity of the samples used by these authors, because we found about the same value for Merck's salicylic acid ("für kalorimetrische Bestimmungen"), and also because I found that this value was altered after purification of the sample. However, later investigations have shown that the sample from Merck, which I used, was an impure one. Another sample, obtained from Merck during 1926, has the same heat of combustion as my purified samples. Verkade and Coops also have burned two of my samples and found the same value as for their original samples. The discrepancy between their value and my own cannot, therefore, be due to impurity of the samples, but must be caused by a systematic error in the determinations.

Verkade and Coops submit that they have no reason to doubt the correctness of their value, because the ratios of the heats of combustion of benzoic acid and naphthalene and of benzoic acid and cane-sugar, determined by themselves, are in full agreement with those which have been obtained in careful work by other authors, and at present are generally accepted. They suggest, therefore, the possibility that in burning naphthalene and cane-sugar I may find other values for these ratios. I cannot believe this to be relevant to the present discussion, which only concerns the ratio of the heats of combustion of benzoic acid and salicylic acid. Presumably it should be easier to determine the exact ratio in the case of the chemically similar substances benzoic acid and salicylic acid than in the case of benzoic acid and the chemically different substances naphthalene and cane-sugar. As is well known, naphthalene has a relatively high vapour pressure and therefore evaporates appreciably even at the ordinary temperature. Cane-sugar, which is completely purified only with difficulty, generally needs auxiliary substances for ignition, and even then incomplete combustion is often the result. As a matter of course, these facts make the heats of combustion of naphthalene and cane-sugar less trustworthy than those of benzoic and salicylic acids, which are not volatile and do not need auxiliary substances for ignition.

## Experimental.

The ratio of the heats of combustion of benzoic and salicylic acids has now been redetermined as follows.

A series of 22 combustions was carried out, under exactly the same conditions, with benzoic acid and salicylic acid alternately, *i.e.*, 11 combustions with each. The quantities of the substances used, about 0·64 and 0·78 g., respectively, always caused an equal rise, of about 1°, in the temperature of the calorimeter, the mean temperature being 19°. An oxygen pressure of 35 atm. was used, as this sufficed for the complete combustion of both substances. The ignition was effected electrically by means of a very thin platinum wire and without the aid of auxiliary substances. A detailed description of the calorimeter and method has recently been published in another journal (*Archiv for Mathematik og Naturvidenskab, Oslo*, 1926, **39**, Nr. 6).

The preparations used in the present investigation are: A standard sample of benzoic acid (39*c*) from the Bureau of Standards, Washington; a sample of benzoic acid (590) purified in the same way as sample 517 in my previous paper; three samples of salicylic acid, 571 II*b*, 572 III, and 572 IV, which were also used in my first investigation; and a sample of salicylic acid "von Heyden," purified by Verkade by crystallising it twice from water and once from chloroform (designated "Verk.").

After the necessary corrections had been applied for loss of heat and for formation of nitric acid, the rise in temperature of the calorimeter was calculated on the basis of 1 g. of the substance (weighed in a vacuum) being burned. The following are the results of the 22 combustions.

*Benzoic Acid.*

| Sample. | Rise in temp. for 1 g. of subst. (vac.). |
|---|---|
| 39*c* | 1·5549°, 1·5549°, |
| ,, | 1·5551 , 1·5550 , |
| ,, | 1·5550 , 1·5550 , |
| ,, | 1·5554 , 1·5548 , |
| ,, | 1·5550 . |
| 590 | 1·5550 , 1·5555 . |
| Mean | 1·55505 |

*Salicylic Acid.*

| Sample. | Rise in temp. for 1 g. of subst. (vac.). |
|---|---|
| 571 II*b* | 1·2883°, 1·2879°. |
| 572 III | 1·2878 , 1·2878 . |
| 572 IV | 1·2883 , 1·2878 . |
| Verk. | 1·2876 , 1·2879 , |
| ,, | 1·2879 , 1·2880 , |
| ,, | 1·2878 . |
| Mean | 1·28792 |

The ratio of the heats of combustion of benzoic acid and salicylic acid is accordingly $1{\cdot}55505/1{\cdot}28792 = 1{\cdot}2074_1$ (vac.). Previously $1{\cdot}2073_4$ (vac.) was found. The mean of the two determinations is $1{\cdot}2073_7$ (vac.). As the heat of combustion of benzoic acid is fixed at 6319 $cal._{15}$. per g. (vac.), the heat of combustion of salicylic acid is 5233·7 $cal._{15}$. per g. (vac.), or 5237·3 per g. (air).

The possible errors arising in this determination will be considered briefly. The accuracy of the measurement of the heat evolved during combustion is dependent only on the accuracy of the determination of the rise in temperature, as the heat capacity of the calorimeter was always the same. Thus the same quantity of water and the same pressure of oxygen were used, and, further, the difference between the heat capacities of the products of combustion and that of the oxygen necessary for the combustion is very nearly the same in the case of the quantities used of the two substances. By means of a trustworthy platinum resistance thermometer the temperature could be read accurately to 0·0001° or less. The correction for loss of heat generally amounted to about 0·2% of the total heat evolved. Even an error of 10% in the calculation of this correction would, therefore, result in an error of only 2 parts per 10,000 in the final result. The heat of formation of nitric acid varied from 0·4 to 0·6 cal. The total corrections in my experiments amounted, accordingly, to only 2—2·5 parts per 1000.

Another cause of error is to be found in the combustion process in the bomb. Here, an error might arise either from incomplete combustion of the substance or from the contamination of the oxygen by combustible impurities. In my experiments, the combustion of the substance was complete, as no soot could be detected in the bomb and no carbon monoxide could be found in the products of combustion. Even very small quantities of carbon monoxide can be detected when about 2 litres of the gaseous products of combustion are collected in a bottle and shaken thoroughly with 15 c.c. of a dilute solution of palladium chloride. I have previously shown that oxygen, prepared from liquid air, often contains small quantities of combustible impurities (see the detailed description), and that special attention should always be paid to the oxygen used in calorimetric work. The oxygen used in the present case was free from such impurities, as ensured by passing it, before it was filled into the bomb, through a heated, thick-walled copper tube filled with palladium asbestos and pieces of platinum.

In conformity with what has been said above, I must abide by the correctness of my value of the ratio of the heats of combustion of benzoic acid and salicylic acid, *viz.*, 1·2074 (vac.).

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[*Received, November 26th,* 1926.]

# LII.—*The Isomerism of Reduced Derivatives of Quinoxaline. Part II. The Stereoisomeric 2 : 3-Dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines.*

By CHARLES STANLEY GIBSON.

LIKE 2 : 3-diphenylquinoxaline (J., 1923, **123**, 1570), 2 : 3-dimethylquinoxaline (Gabriel and Sonn, *Ber.*, 1907, **40**, 4852), on reduction with sodium and ethyl alcohol, yields a mixture of two 2 : 3-disubstituted 1 : 2 : 3 : 4-tetrahydroquinoxalines, $C_6H_4<\begin{matrix}NH\cdot CHMe\\ NH\cdot CHMe\end{matrix}$. These two bases may be separated by taking advantage of the fact that the oxalate and the picrate of the externally compensated base are both less soluble than the corresponding salts of the *meso*-base.

The *meso*-base has been examined and characterised by the preparation of a number of simple derivatives. The externally compensated base has been resolved by means of *d*- and *l*-tartaric acids, which have, in this case, proved more useful than the stronger acids derived from optically active camphor. Whilst enantiomorphism in the crystalline form of the optically active bases has again been demonstrated, the analogy to the stereoisomerism of the tartaric acids is not so complete in this case as in the former, since the externally compensated base now described is probably a pseudo-racemic mixture, the melting points of all mixtures of the two optically active bases being between the melting point of the optically active bases and that of the externally compensated base. The rotatory powers of the bases are markedly higher than those of the corresponding 2 : 3-diphenyl derivatives previously described and the acyl derivatives possess considerable rotatory powers opposite in sign to those of the optically active bases from which they are prepared.

The following is a summary of the constants of the more important compounds now described :

| | M. p. | $[M]^{20°}_{5461}$. |
|---|---|---|
| *l*-2 : 3-Dimethyltetrahydroquinoxaline ..... | 94·5° | −181·4° |
| *d*-2 : 3-Dimethyltetrahydroquinoxaline ..... | 94·5 | +181·9 |
| *dl*-2 : 3-Dimethyltetrahydroquinoxaline ..... | 101—102 | — |
| *meso*-2 : 3-Dimethyltetrahydroquinoxaline ..... | 111—112 | — |
| 1-Benzoyl derivative of *l*-base ..... | 233—234 | +983·3 |
| 1-Benzoyl derivative of *d*-base ..... | 233—234 | −981·7 |
| 1-*p*-Toluenesulphonyl derivative of *l*-base ..... | 172—173 | +211·3 |

## EXPERIMENTAL.

### meso-2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline.*

2 : 3-Dimethylquinoxaline was prepared in considerable quantities from diacetyl and *o*-phenylenediamine as described by Gabriel and

Sonn (*loc. cit.*). It was purified by steam distillation, and crystallised from the hot distillate in long, prismatic needles which probably contain three molecules of water of crystallisation (Found : $H_2O$, 24·6. $C_{10}H_{10}N_2,3H_2O$ requires $H_2O$, 25·5%). The anhydrous compound melts at 104·5—105·5° (compare Gabriel and Sonn).

The most satisfactory method of reducing the above base is by means of sodium in boiling absolute ethyl-alcoholic solution. The base (10 g.) was dissolved in boiling ethyl alcohol (300 c.c.) and sodium (25 g.) introduced in small lumps, a further small quantity of alcohol being used if necessary to facilitate the solution of the last portions of sodium. The alcoholic solution from two experiments was allowed to cool and acidified with concentrated hydrochloric acid (170 c.c.), the sodium chloride filtered off, and the filtrate and washings were evaporated to dryness. The residue was dissolved in dilute hydrochloric acid and the reduced mixed bases were precipitated by means of excess of sodium hydroxide, filtered off, washed with water, and dried in a vacuum desiccator; a further small quantity of the mixed bases was obtained by extraction of the alkaline solutions with ether (total yield, 175 g. from 190 g. of 2 : 3-dimethylquinoxaline).

In the earlier experiments, it had been proved that when equivalent quantities of the reduced mixed bases and picric acid were mixed in alcoholic solution, the picrate of what was subsequently shown to be *dl*-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline was very much less soluble than that of the *meso*-base. Under certain conditions, however, which were not fully investigated, the base liberated from the less soluble picrate was contaminated with a deep red base, indicating that oxidation had taken place. Subsequently it was found possible to separate the two bases in a state of greater purity and more easily by means of oxalic acid, the oxalate of the externally compensated base being again the less soluble in ethyl alcohol.

12·4 G. (1 mol.) of the mixed bases dissolved in boiling ethyl alcohol (120 c.c.) were mixed with 9·7 g. (1 mol.) of crystalline oxalic acid dissolved in 40 c.c. of hot alcohol. The crystalline oxalate (p. 346) which separated was filtered off when the solution had stood for some hours. The alcoholic filtrate was evaporated to dryness, the residue suspended in water, basified with ammonia, and the base extracted thoroughly with benzene. The base obtained on evaporation of the benzene solution was repeatedly crystallised from benzene–ligroin and finally from alcohol until its melting point was no longer altered. It was obtained in almost colourless plates, m. p. 111—112°. Under these conditions, this internally compensated base forms approximately 75% of the reduction product

of 2 : 3-dimethylquinoxaline (Found: C, 73·9; H, 8·9. $C_{10}H_{14}N_2$ requires C, 74·0; H, 8·7%).

meso-2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was examined crystallographically by Dr. G. M. Bennett of the University of Sheffield, to whom I am very greatly indebted for the crystallographic reports in the present paper. It crystallises in the monoclinic system with $a : b : c = ? : 1 : 0{\cdot}625$; $\beta = 91°\ 5'$. Large, flat, rhomb-shaped crystals were obtained from acetone, developed on $a(100)$ and bounded by the form $m(011)$, but they were somewhat irregular and the angular values are only approximate:

| | $a(100)$. | $m(011)$. | $m'(01\bar{1})$. |
|---|---|---|---|
| $\phi$ ..... | 0° 0′ | *88° 16′ | *268° 16′ |
| $\rho$ ..... | 90° 0′ | *32° 2′ | 32° 2′ |

There is a perfect cleavage in the plane $a(100)$. The extinction on $a$ is along the diagonal, which confirms the position of the plane of symmetry, and the crystals are biaxial.

meso-1 : 4-*Diacetyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, $C_6H_4<\begin{matrix}NAc\cdot CHMe\\ NAc\cdot CHMe\end{matrix}$, was prepared by heating the base with an excess of acetic anhydride on the water-bath for 1 hour. It crystallises from hot water in long, colourless needles, m. p. 145—146° (Found: C, 68·2; H, 7·3. $C_{14}H_{18}O_2N_2$ requires C, 68·25; H, 7·4%).

meso-1 : 4-*Dibenzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by the Schotten-Baumann method, using a considerable excess of benzoyl chloride. It crystallises from ethyl alcohol in thin, colourless prisms, m. p. 218·5—219·5° (Found: C, 77·4; H, 6·4; N, 7·6. $C_{24}H_{22}O_2N_2$ requires C, 77·8; H, 6·0; N, 7·6%).

The following compounds were obtained by treating the base with the acyl chloride in pyridine and isolating the product in the usual manner.

meso-1-*Benzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* is much more soluble in alcohol than the dibenzoyl derivative, a small quantity of which is always obtained at the same time. It crystallises from alcohol in colourless, massive prisms, m. p. 137—138° (Found: C, 77·0; H, 6·9; N, 11·1. $C_{17}H_{18}ON_2$ requires C, 76·6; H, 6·8; N, 10·5%). It yields a colourless hydrochloride sparingly soluble in water and an almost colourless nitroso-compound which begins to decompose without melting at about 140°.

meso-1 : 4-*Di*-m-*nitrobenzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* crystallises from chloroform–ethyl alcohol in very pale yellow needles, m. p. 243—244° (Found: C, 62·6; H, 4·5. $C_{24}H_{20}O_6N_4$ requires C, 62·6; H, 4·4%).

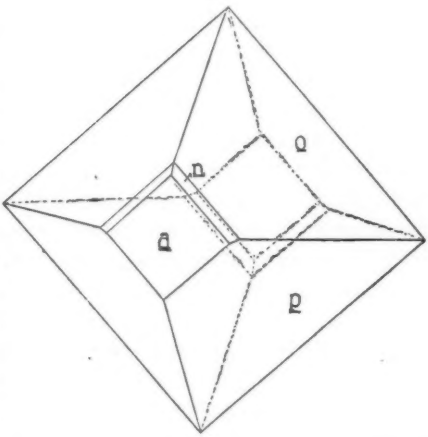
meso-1-p-*Nitrobenzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinox-*

*aline* crystallises from ethyl alcohol in red needles, m. p. 167° (Found: C, 65·55; H, 5·55. $C_{17}H_{17}O_3N_3$ requires C, 65·5; H, 5·5%).

meso-1-p-*Toluenesulphonyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* crystallises from ethyl alcohol in colourless prisms, m. p. 183—184° (Found: C, 64·55; H, 6·3. $C_{17}H_{20}O_2N_2S$ requires C, 64·5; H, 6·4%).

meso-1 : 4-*Diphenylcarbamyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by keeping the base and an excess of phenylcarbimide in purified and dry acetone solution for some 12 hours. The product was repeatedly crystallised from purified acetone and obtained in colourless, soft needles, m. p. 190—191° (Found: C, 71·9; H, 5·9; N, 14·2. $C_{24}H_{24}O_2N_4$ requires C, 72·0; H, 6·0; N, 14·0%).

FIG. 1.




meso-1-*Carbamyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* was prepared by adding potassium cyanate (2 g.) gradually to a warm solution of the base (2 g.) in the calculated quantity of *N*/2-hydrochloric acid. The crystalline precipitate which separated in almost theoretical quantity was dried and recrystallised from benzene. Well-developed crystals were obtained, m. p. 162—163° (Found: C, 64·6; H, 7·25; N, 20·5. $C_{11}H_{15}ON_3$ requires C, 64·4; H, 7·4; N, 20·5%). Dr. Bennett's crystallographic report is:

This substance crystallises in the holohedral class of the monoclinic system with $a : b : c = 0{\cdot}9131 : 1 : 0{\cdot}9429$; $\beta = 92° 16'$. It is thus pseudo-cubic and the habit of the crystals from benzene solution is octahedral, the forms developed being $a(100)$, $n(311)$, $o(111)$, $p(\bar{1}11)$, $o'(1\bar{1}1)$ as shown in Fig. 1. The following mean angular values were obtained from three selected crystals:

| | $a(100)$. | $n(311)$. | $o(111)$. | $p(\bar{1}11)$. | $o'(1\bar{1}1)$. | $p(1\bar{1}\bar{1})$. |
|---|---|---|---|---|---|---|
| $\phi$ ..... | 0° 0′ | 21° 38′ | *52° 2′ | 126° 40′ | * 4° 20′ | 354° 58′ |
| $\rho$ ..... | 90° 0′ | 90° 0′ | 90° 0′ | 90° 0′ | *38° 7′ | 36° 42′ |

No marked cleavage was observed. Optical examination confirms the fact that the crystals are biaxial. The extinction on the face

*a* coincides with the diagonal of the face and an optic bisectrix emerges perpendicular to *a*.

*Resolution of Externally Compensated* 2 : 3-*Dimethyltetrahydroquinoxaline into its Optically Active Components.*

The crystalline oxalate * (p. 343) was suspended in water and treated with an excess of a solution of ammonia. Thorough extraction with benzene then removed a base, which was recrystallised from ligroin (b. p. 40—60°) until its melting point was unchanged. The almost colourless crystals had m. p. 101—102°, and the melting points of mixtures of this and the *meso*-base were always below 100°.

That the base having m. p. 101—102° is the externally compensated base, *dl*-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline, was proved in a preliminary experiment by resolving 2 g. of the base by means of an equimolecular quantity of *d*-α-bromocamphor-π-sulphonic acid in aqueous solution, ethyl alcohol being added in small quantities to prevent the too rapid crystallisation of any salt at the ordinary temperature. After some hours, a salt (*d*A,*l*B) was obtained and from this, without further purification, the base was liberated. This base, after one crystallisation from ligroin (b. p. 40—60°), had $[\alpha]_{5461} = -84{\cdot}5°$ in 0·5% ethyl-alcoholic solution; the base liberated from the mother-liquor from the above salt had $[\alpha]_{5461} = +45{\cdot}3°$ under similar conditions. Whilst this experiment served to prove that the base having m. p. 101—102° is the externally compensated base, the resolution could not be repeated. No fewer than twelve experiments were performed in which every effort was made to maintain the conditions of the successful experiment, but in all cases the crystalline salt yielded a base which was optically inactive. With *d*-camphor-β-sulphonic acid under analogous conditions, positive indications of the partial resolution of this base were repeatedly obtained, but the rotatory power of the base from the repeatedly recrystallised, less soluble salt was very much smaller than that observed in the first successful experiment. Similarly, attempts to resolve the base by means of *d*-α-bromocamphor-β-sulphonic acid, *d*-benzoylalanine and *d*-hydroxymethylenecamphor were tried without success.

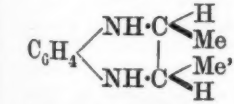
The resolution of the base by means of *d*- and *l*-tartaric acids was immediately successful. The following describes a typical experiment. *d*-Tartaric acid (20·0 g.; 1 mol.) was dissolved in boiling water (350 c.c.), and the base (21·4 g.; 1 mol.) dissolved in the boiling solution, which was then left to cool in the ice-chest for some

* In the first experiments the *dl*-2 : 3-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoxaline was liberated from the less soluble picrate. The base so obtained was identical in all respects with that obtained from the less soluble oxalate.

hours. The salt (16·9 g.; 80% of the theoretical quantity) crystallised in long, colourless needles and yielded a base which in a 0·6% ethyl-alcoholic solution had $[\alpha]_{5461} = -90·4°$. The crystalline salt was therefore the *d*A,*l*B salt. The crude base (13·0 g.) obtained from the mother-liquor was treated with an equivalent quantity (12·0 g.) of *l*-tartaric acid (obtained by resolving racemic acid in the manner described by Marckwald, *Ber.*, 1896, **29**, 42) under exactly similar conditions to the above. The salt (15·5 g.), *l*A,*d*B, was similar in properties to the salt previously obtained, and yielded a base which in 0·6% ethyl-alcoholic solution had $[\alpha]_{5461} = +97·2°$. The base recovered from the mother-liquor from the *l*A,*d*B salt amounted to 4·85 g., so that practically the whole of the base originally taken was accounted for.

In order to obtain the optically pure *l*-base, the various specimens of recrystallised *l*-base whose rotatory powers in ethyl alcohol varied from $[\alpha]_{5461} = -96·2°$ to $-90·4°$ were mixed and added gradually to rather more than the equivalent quantity of pure *d*-tartaric acid, dissolved in sufficient boiling water, so that the whole remained dissolved at the boiling point. This solution was rapidly filtered and the filtrate left to crystallise. Pure l-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* d-*tartrate*, $C_{10}H_{14}N_2,C_4H_6O_6,2H_2O$, separated, on cooling, in characteristic, long, colourless needles which were separated in the usual manner. The anhydrous salt begins to decompose at about 149° (Found: $H_2O$, 10·5. $C_{14}H_{20}O_6N_2,2H_2O$ requires $H_2O$, 10·4%. Found in anhydrous material: C, 54·0; H, 6·7. $C_{14}H_{20}O_6N_2$ requires C, 53·8; H, 6·5%). The salt cannot be conveniently recrystallised, as its solutions darken somewhat rapidly. Its rotatory power was determined in ethyl-alcoholic solution at 20°: $c = 1·03$, $l = 4$, $\alpha_{5461} = -2·07°$, $[\alpha]_{5461} = -50·2°$.

Pure d-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline* l-*tartrate* was obtained in a similar manner from the recrystallised specimens of the not quite completely resolved *d*-base and pure *l*-tartaric acid. It had analogous properties (Found in anhydrous material: C, 54·1; H, 6·8. $C_{14}H_{20}O_6N_2$ requires C, 53·8; H, 6·5%). Its rotatory power was determined in ethyl-alcoholic solution at 20°: $c = 1·004$, $l = 4$, $\alpha_{5461} = +2·00°$, $[\alpha]_{5461} = +49·9°$.

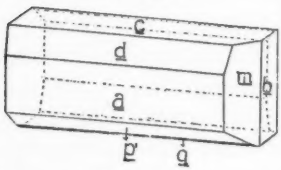
l- *and* d-2 : 3-*Dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalines*,  , were obtained in each case from the corresponding pure tartrate. The salt was suspended in water, a slight excess of ammonia added, and the mixture extracted thoroughly with

benzene. The benzene solution after washing and drying was evaporated to dryness, and the residue extracted carefully with redistilled ligroin (b. p. 40—60°) in a Soxhlet apparatus. The pure base was obtained in massive, but distorted, almost colourless prisms. The pure bases have m. p. 94·5° and melting points of mixtures of the two bases lie between this melting point and the melting point of the externally compensated base (101—102°). The solubility of the active bases in organic solvents is high and distinctly greater than that of the externally compensated base. These bases are most conveniently recrystallised from ligroin [Found: (*l*-base) C, 74·1; H, 8·8; (*d*-base) C, 74·0; H, 9·1. $C_{10}H_{14}N_2$ requires C, 74·0; H, 8·7%]. The rotatory powers were determined in ethyl-alcoholic solution at 20°:

*l*-base: $c = 0{\cdot}6024$, $l = 4$, $\alpha_{5461} = -2{\cdot}70°$, $[\alpha]_{5461} = -112{\cdot}0°$.
*d*-base: $c = 0{\cdot}5902$, $l = 4$, $\alpha_{5461} = +2{\cdot}65°$, $[\alpha]_{5461} = +112{\cdot}3°$.

Although crystals of both the *l*- and the *d*-base were obtained after considerable trouble by the slow evaporation of their solutions in pure acetone, only those of the *d*-base, examined by Dr. Bennett, need be described.

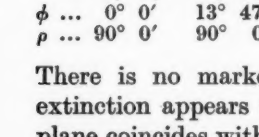
FIG. 2.




*d*-2:3-Dimethyl-1:2:3:4-tetrahydroquinoxaline crystallises in the sphenoidal class of the monoclinic system with $a : b : c = 1{\cdot}362 : 1 : 0{\cdot}892$; $\beta = 91°\ 56'$. The forms observed were *a*(100), *c*(001), *b*(010), *m*(110), *p*($\bar{1}$01), *q*($\bar{3}$05), *d*(601). Some crystals are simple combinations of *m* and *c*, but others show the definitely enantiomorphous habit depicted in Fig. 2, with elongation along the *b* axis. Owing to the imperfections of the crystals some of the following mean angular values (obtained from five crystals) are a little uncertain:

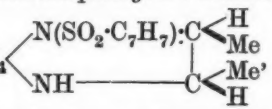
| | *a*(100) | *d*(601) | *c*(001) | *q*($\bar{3}$05) | *p*($\bar{1}$01) | *m*(110) | *b*(010) |
|---|---|---|---|---|---|---|---|
| $\phi$ ... | 0° 0′ | 13° 47′ | *88° 4′ | 109° 15′ | *121° 54′ | 0° 0′ | 0° 0′ |
| $\rho$ ... | 90° 0′ | 90° 0′ | 90° 0′ | 90° 0′ | 90° 0′ | *36° 18′ | −0° 6′ |

There is no marked cleavage. The substance is biaxial. The extinction appears to be straight on *a* and *c*, and the optic axial plane coincides with *b*.

1-1-*Benzoyl*-2:3-*dimethyl*-1:2:3:4-*tetrahydroquinoxaline*,  , was prepared by treating a solution of the *l*-base (1·5 g.) with a benzene solution of benzoyl chloride (3 g.) and

sodium hydroxide in the usual manner at the ordinary temperature. The product was recrystallised three times from benzene, its m. p., 233—234° (decomp.), not altering after the first crystallisation. It was obtained in small, colourless needles (Found: N, 10·5. $C_{17}H_{18}ON_2$ requires N, 10·5%). Its rotatory power was determined at 20° in ethyl alcohol, in which solvent the substance is only sparingly soluble: $c = 0{\cdot}2338$, $l = 4$, $\alpha_{5461} = +3{\cdot}46°$, $[\alpha]_{5461} = +369{\cdot}7°$.

d-1-*Benzoyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 233—234° (decomp.), was obtained in a precisely similar way from the *d*-base, and the compound has analogous properties (Found: C, 76·4; H, 6·7; N, 10·4. $C_{17}H_{18}ON_2$ requires C, 76·6; H, 6·8; N, 10·5%). Its rotatory power was determined in ethyl-alcoholic solution at 20°: $c = 0{\cdot}3596$, $l = 4$, $\alpha_{5461} = -5{\cdot}31°$, $[\alpha]_{5461} = -369{\cdot}1°$.

l-1-p-*Toluenesulphonyl*-2 : 3-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*,  , was prepared from the *l*-base (1·5 g.) and *p*-toluenesulphonyl chloride (3·7 g.) in pyridine solution. The product crystallised from alcohol in small, colourless plates, m. p. 172—173° (decomp.) (Found: N, 8·6. $C_{17}H_{20}O_2N_2S$ requires N, 8·9%). Its rotatory power was determined in ethyl alcohol at 20°: $c = 0{\cdot}5762$, $l = 4$, $\alpha_{5461} = +1{\cdot}54°$, $[\alpha]_{5461} = +66{\cdot}9°$.

I wish to express my thanks to the Government Grant Committee of the Royal Society for a grant which has covered the cost of the materials used in this investigation and to the workers in my laboratory who have made it possible for me to complete this part of the investigation.

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S.E. 1.

[*Received, December 13th*, 1926.]

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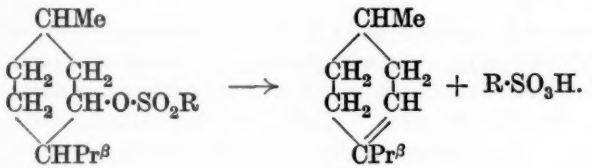
## LIII.—*The Decomposition Products of Menthyl Esters of Sulphonic Acids.*

By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE.

WHILE engaged in an examination of the optical rotation of menthyl benzenesulphonate and menthyl naphthalene-β-sulphonate, Patterson and Frew (J., 1906, **89**, 332) noticed that these compounds decompose at temperatures just above their melting points, both in the homogeneous state and in nitrobenzene solution, whereas

many other menthyl esters are much more stable, and are distillable at considerably higher temperatures. We have recently investigated this decomposition more fully and have found that, on direct distillation of menthyl benzene- and naphthalene-α- and -β-sulphonates under reduced pressure, the main reaction is decomposition into menthene and the corresponding sulphonic acid according to the equation

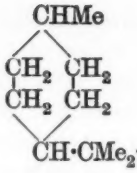


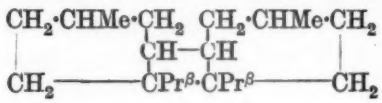

But when the heating of the homogeneous ester is carried out in sealed tubes at ordinary pressure, secondary decompositions take place with formation of hexahydrocymene, carbonaceous matter, and tarry products, whilst the menthene which is possibly first formed polymerises to dimenthene and a more complex gelatinous substance. None of the menthene appears to survive, if indeed it is formed at all.

## EXPERIMENTAL.

*Menthyl benzenesulphonate* (m. p. 80°) was prepared as described in the paper quoted above, and was then decomposed in various ways.

I. On heating the ester at 85—90° for 6 hours in a tube, which, although no pressure developed, was sealed, complete separation into two layers took place. On cooling, the lower brown layer solidified to form a low-melting, deliquescent solid. The upper layer in the crude condition had a slight positive rotation; it was separated, by distillation at 4 mm. pressure, into two fractions of b. p. 72—75° and 150—240°. The lower-boiling fraction (A) was a clear, colourless, optically-inactive liquid, distilling at ordinary pressure from 167—169° (Found: C, 85·7, 85·6; H, 14·4, 14·4; *M*, cryoscopic in benzene, 142. $d_4^{17°}$ 0·7962, $n_D$ 1·44009; whence $[R_L]_D = 46·35$. $C_{10}H_{20}$ requires C, 85·7; H, 14·3%; *M*, 140). The substance appears thus to be a saturated ring compound. With nitric acid (*d* 1·075), a yellow nitro-derivative was obtained, b. p. 135—137°/25 mm., $n_D$ 1·46241, presumably therefore tertiary nitromenthane (I). The original liquid thus appears to be hexahydrocymene, which has been shown to form a tertiary nitro-compound corresponding to that which we obtained (Konowalov, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 237).

(I.) 

(II.) 

The higher-boiling fraction was separated by distillation under reduced pressure into a viscous, oily liquid (B), b. p. 174°/4 mm., and a gelatinous mass (C), b. p. 240—270°/4 mm. The fraction (B) (Found: C, 86·8, 86·8; H, 13·2, 13·15; *M*, cryoscopic in benzene, 273·1. $d_4^{17°}$ 0·8845, $n_D$ 1·48704; whence $[R_L]_D = 88·14$. $C_{20}H_{36}$ requires C, 86·9; H, 13·1%; *M*, 276; $[R_L]_D$, 87·96) had a slight dextrorotation, $[\alpha]_{5461}^{17°}$ (*c* = 5 in benzene) = +2·29°, and did not decolorise potassium permanganate solution on standing; on treatment with bromine, hydrogen bromide was evolved. This compound closely approximates to that obtained by Tolloczko (*J. Russ. Phys. Chem. Soc.*, 1897, **29**, 39; *Chem. Zentr.*, 1898, **I**, 105) by treating menthol with sulphuric acid (except that his product was completely inactive), and thus appears to be dimenthene (II) (Kanonnikov, *Chem. Zentr.*, 1899, II, 860). A gelatinous compound corresponding to that (C) obtained by us was also observed by Tolloczko. Owing to the difficulty of purifying this compound, we have been unable to identify it.

*Solid product.* The solid substance constituting the lower layer after the heating of menthyl benzenesulphonate was deliquescent and of low melting point. We were unable to crystallise it from any solvent. It was easily soluble in water and the solution gave a strongly acid reaction. The barium salt prepared from the aqueous solution after boiling with animal charcoal was purified by recrystallisation from water [Found: $H_2O$, 3·9, 3·9; Ba, 29·0, 29·0. Calc. for $Ba(SO_3·C_6H_5)_2,H_2O$: $H_2O$, 3·8; Ba, 29·3%]. The solid substance which separates on heating menthyl benzenesulphonate is therefore mainly, or exclusively, benzenesulphonic acid.

II. *Decomposition by Direct Distillation.*—If, instead of being heated in a sealed tube, menthyl benzenesulphonate be directly distilled at a pressure of 4 mm., a vapour condensing to a colourless liquid passes over at 68° (the substance, heated in an oil-bath, being meanwhile at a temperature a little above its melting point), and a brown, deliquescent solid remains in the flask.

The liquid (D) boiled at 165° under ordinary pressure and had the rotation $[\alpha]_{5461}^{20°} = +9·56°$ (Found: C, 86·8, 86·8; H, 13·15, 13·2; *M*, cryoscopic in benzene, 138·4. $C_{10}H_{18}$ requires C, 86·9; H, 13·1%; *M*, 138. $d_4^{17°}$ 0·8130, $n_D$ 1·45162; whence $[R_L]_D = 45·72$. Calc. for $C_{10}H_{18}$ + one ethylene linking, 45·71). It formed a nitroso-

chloride, m. p. 117°, and thus appears to be the same menthene as obtained by Zelikov (*Ber.*, 1904, **37**, 1374) by the action of various dibasic acids such as succinic acid, tartaric acid, citric acid, phthalic acid, terephthalic acid on menthol at high temperatures, and by Tschugaev (*Ber.*, 1899, **32**, 3332) by distilling menthyl xanthates in a vacuum. The rotation of the menthene formed in such experiments varies greatly; that obtained by Tschugaev had the high rotation $[\alpha]_D = 114{\cdot}77°, 116{\cdot}06°$, which may have been due to the fact that his menthyl xanthate had a fairly low melting point, 39°.

In our experiment the higher-boiling dimenthene does not appear to be formed, whilst the other product of decomposition was found, from analysis of its barium salt, to be benzenesulphonic acid.

III. *Decomposition in Solution.*—Patterson and Frew (*loc. cit.*) had already noticed that menthyl benzenesulphonate also decomposed on heating in nitrobenzene solution. We ascertained that, when it is heated in benzene solution under reflux, little decomposition takes place, whereas in toluene decomposition appears to be complete. A brown solid separated which proved to be benzenesulphonic acid; the toluene solution acquired a positive rotation, and, after distillation of the solvent, a fraction was obtained, b. p. 190°/20 mm., presumably dimenthene. No lower-boiling decomposition product appeared to be formed.

I. *Menthyl naphthalene-β-sulphonate* (m. p. 114·5°), which had been examined by Patterson and Frew, was prepared again and heated in a sealed tube at 120°. Decomposition took place, and, as in the case of the benzenesulphonate, three distillable liquids were obtained. The most easily volatile fraction (A) boiled between 167° and 169° under ordinary pressure (Found: C, 85·75, 85·6; H, 14·2, 14·4%). The liquid was inactive and was identical with the hexahydrocymene obtained from menthyl benzenesulphonate.

The middle fraction, b. p. 174°/4 mm., had a slight positive rotation (Found: C, 86·8, 86·7; H, 13·1, 13·2%). It was the same as the dimenthene, $C_{20}H_{36}$, obtained from the benzenesulphonic ester. Some of the gelatinous substance, b. p. 240—270°/4 mm., was also obtained, but was not further examined.

In this case the solid which was produced on heating crystallised with difficulty from chloroform; m. p. 80°. From it a barium salt was prepared crystallising in flat, glistening plates [Found: $H_2O$, 3·2, 3·2; Ba, 24·1, 24·0. Calc. for $(C_{10}H_7{\cdot}SO_3)_2Ba,H_2O$: $H_2O$, 3·2; Ba, 24·1%]. The decomposition product is therefore naphthalene-β-sulphonic acid.

II. When menthyl naphthalene-β-sulphonate, instead of being heated in a sealed tube, was distilled directly under 4 mm. pressure, a liquid boiling at 68° passed over and a yellow solid residue was

left in the flask. The liquid boiled at 165° under ordinary pressure, had a positive rotation of $[\alpha]^{20°}_{5461} = +9{\cdot}4°$, and on analysis gave values corresponding to the formula $C_{10}H_{18}$, proving it to be the menthene obtained in the corresponding experiment with menthyl benzenesulphonate. The solid was naphthalene-β-sulphonic acid, which was characterised by the analysis of its barium salt.

III. Menthyl naphthalene-β-sulphonate, heated in nitrobenzene solution at 100° or in xylene solution at 120°, decomposed and, on cooling, naphthalene-β-sulphonic acid separated. The reaction products were not further examined.

I. *Menthyl naphthalene-α-sulphonate* (m. p. 116·5°, decomp.) was prepared in 60% yield in the same way as the other two sulphonic esters, and was crystallised from alcohol. It is soluble in most common solvents and has $[\alpha]^{17·5°}_{5461}$ (in benzene; $c = 1$) $= -93{\cdot}25°$ and $[\alpha]^{17·5°}_{5461}$ (in alcohol; $c = 1$) $= -114{\cdot}8°$.

When it was decomposed in a sealed tube at 120°, two layers were formed. The liquid, on distillation and analysis, yielded the same three fractions as before, namely, hexahydrocymene (b. p. 167—169°/ordinary pressure. Found: C, 85·6; H, 14·4%); dimenthene (b. p. 174°/4 mm. Found: C, 86·6; H, 13·1%), and a gelatinous mass boiling from 240—270°/4 mm. The lower layer consisted of naphthalene-α-sulphonic acid, as was proved by the analysis of its barium salt [Found: Ba, 24·2, 24·1. Calc. for $(C_{10}H_7{\cdot}SO_3)_2Ba,H_2O$: Ba, 24·1%].

II. On decomposition of this ester by direct distillation in a vacuum, menthene and naphthalene-α-sulphonic acid were the only products obtained and were characterised as before.

III. The ester also decomposed when heated in solution in much the same way as in the other two cases.

UNIVERSITY OF GLASGOW. [*Received, December 23rd,* 1926.]

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## LIV.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part XXIV.* Menthyl Benzenesulphonate, Menthyl Naphthalene-α-sulphonate, and Menthyl Naphthalene-β-sulphonate in Various Solvents.*

By THOMAS STEWART PATTERSON and IRENE MARY MCALPINE.

WE have examined the rotations of the esters described in the foregoing paper for three different colours of light, mercury yellow ($\lambda = 5790$), mercury green ($\lambda = 5461$), mercury violet ($\lambda = 4358$),

* Pt. XXIII, J., 1916, **109**, 1204.

and in several solvents which, for convenience of reference, are indicated by letters of the alphabet, namely, (*a*) ethyl alcohol; (*b*) benzene; (*c*) pyridine; (*d*) nitrobenzene; (*e*) ethylene dibromide; (*f*) quinoline. Since the object of our investigation was, in the first place, to obtain a general oversight, we examined only one solution in each case at a concentration between 4·45 and 1. The data are given in the tables of specific rotations.

TABLE I.

*Specific Rotations of Menthyl Sulphonates in Various Solvents.*

$t$ = approximately 17·5° throughout.

Menthyl benzenesulphonate.

| Solvent ..... | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| Concentration | 4·0 | 4·5 | 4·0 | 4·0 | 4·0 | 3·0 |
| y ..... | − 74·7° | − 65·5° | − 67·9° | − 67·4° | − 72·7° | − 64·4° |
| g ..... | − 84·6 | − 74·0 | − 76·3 | − 75·9 | − 82·6 | − 72·8 |
| v ..... | −142·2 | −123·2 | −127·4 | −127·9 | −137·6 | −122·8 |

Menthyl naphthalene-α-sulphonate.

| Solvent ..... | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| Concentration | 1·0 | 1·0 | 1·0 | 3·0 | 1·0 | 3·0 |
| y ..... | −101·8° | − 81·4° | − 87·3° | − 92·2° | −145·2° | − 84·8° |
| g ..... | −114·8 | − 93·2 | − 98·4 | −104·6 | −163·5 | − 97·2 |
| v ..... | −194·3 | −158·1 | −166·0 | −178·1 | −276·2 | −167·1 |

Menthyl naphthalene-β-sulphonate.

| Solvent ..... | a | b | c | d | e | f |
|---|---|---|---|---|---|---|
| Concentration | 1·0 | 1·0 | 1·0 | 3·0 | 1·0 | 3·0 |
| y ..... | − 56·1° | − 51·9° | − 47·7° | − 43·9° | − 49·3° | − 31·2° |
| g ..... | − 64·0 | − 59·3 | − 55·0 | − 48·7 | − 56·3 | − 35·1 |
| v ..... | −108·0 | −101·9 | − 92·2 | − 82·6 | − 95·7 | − 59·1 |

Although the rotations vary considerably in each case with change of solvent, the change is not sufficient to cause any overlapping, so that the solutions of each substance form a separate group, the rotations of menthyl naphthalene-β-sulphonate being lowest, and those for menthyl naphthalene-α-sulphonate being highest. The rotations for the benzenesulphonate solutions lie wholly between the others. It may also be noticed that the different solvents do not influence the rotations in the same way, although there is some similarity. Quinoline, which usually has a powerful influence either towards exaltation or depression, produces the lowest rotation in menthyl naphthalene-α-sulphonate and in menthyl benzenesulphonate, and the second lowest in menthyl naphthalene-β-sulphonate. Ethylene dibromide, on the other hand, which usually has a powerful influence of the opposite character to quinoline, produces the highest rotation in menthyl naphthalene-α-sulphonate, the second highest in menthyl benzenesulphonate, and the third highest in menthyl naphthalene-β-sulphonate. On the whole, therefore, this general tendency is recognisable.

These values were then plotted on a characteristic diagram and lay with good agreement along lines intersecting one another very close to the point of origin of the diagram, and in such a way, as far as can be judged when extrapolation has to be carried out through some 35° of rotation, as to indicate little or no region of anomalous rotation dispersion. The data thus present a behaviour which we think is rare and it follows that the dispersion coefficients for all these compounds calculated by the ordinary method ought to be almost the same throughout. (For a general discussion of this subject, see J., 1916, **109**, 413.) That this is the case is shown by the following table of dispersion ratios.

TABLE II.

| | Menthyl benzene-sulphonate. Dispersion. | | Menthyl naphthalene-α-sulphonate. Dispersion. | | Menthyl naphthalene-β-sulphonate. Dispersion. | |
|---|---|---|---|---|---|---|
| Solvent. | $Hg_v/Hg_g$. | $Hg_y/Hg_g$. | $Hg_v/Hg_g$. | $Hg_y/Hg_g$. | $Hg_v/Hg_g$. | $Hg_y/Hg_g$. |
| Alcohol ..... | 1·680 | 0·883 | 1·692 | 0·887 | 1·687 | 0·878 |
| Benzene ..... | 1·664 | 0·884 | 1·695 | 0·873 | 1·716 | 0·875 |
| Pyridine ..... | 1·669 | 0·890 | 1·686 | 0·887 | 1·676 | 0·859 |
| Nitrobenzene ... | 1·685 | 0·888 | 1·703 | 0·881 | 1·698 | 0·902 |
| Ethylene dibromide ..... | 1·665 | 0·879 | 1·689 | 0·888 | 1·700 | 0·876 |
| Quinoline ..... | 1·685 | 0·885 | 1·709 | 0·872 | 1·683 | 0·889 |

These data, we think, form an almost unique example of constancy of ordinary dispersion ratios for a series of related substances, the rotation of which, for mercury green, varies over so wide a range as −35·1° for menthyl naphthalene-β-sulphonate in pyridine, up to −163·5° for menthyl naphthalene-α-sulphonate in ethylene dibromide.

The thanks of one of us (I. M. McA.) are due to the Department of Scientific and Industrial Research for a maintenance grant which enabled the work described in this and the preceding paper to be carried out.

UNIVERSITY OF GLASGOW. [*Received, December 23rd*, 1926.]

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## LV.—*The Quantitative Estimation of Mixtures of Isomeric Unsaturated Compounds. Part I. A Bromine Addition Method.*

By REGINALD PATRICK LINSTEAD.

ALTHOUGH the structural conditions necessary to promote the movement of the double bond in the three-carbon system (Birch, Kon, and Norris, J., 1923, **123**, 1361, and subsequent papers by

Kon and his collaborators) have been studied, the quantitative aspect of the subject has been somewhat neglected owing to the difficulty of analysing the mixtures of isomerides obtained. Examination of the position of equilibrium in systems possessing retarded mobility (Kon and Linstead, J., 1925, **127**, 815) would, however, enable the effects of various substituent groups to be compared and the figures thus obtained would be of interest for comparison with the Thorpe-Ingold values for valency distortion and with the values for the *o*-, *p*-, and *m*-directing powers of the same groups when substituted in the benzene nucleus (compare Ingold, Shoppee, and Thorpe, J., 1926, 1477).

In the determination of the position of equilibrium in a three-carbon system,

$$\underset{\alpha\beta\text{-form}}{HC{-}C{=}CX} \qquad \underset{\beta\gamma\text{-form}}{C{=}C{-}CHX}$$

the isomerides present in the equilibrium mixture must first be isolated under conditions precluding further change and their proportion can then be estimated either by physical separation of the individuals, by optical measurements, or by separation through derivatives. The results so obtained are not completely trustworthy and the best methods at present available are those based upon the selective action of reagents such as dilute sulphuric acid (Fittig, *Annalen*, 1894, **283**, 47) and hypoiodous acid (Bougault, *Ann. Chim.*, 1908, **14**, 145), both of which are stated to combine with $\beta\gamma$-unsaturated acids but not with the $\alpha\beta$-isomerides.

The principle of the new method herein described is that the composition of a mixture of $\alpha\beta$- and $\beta\gamma$-isomerides can be determined by comparing its velocity of addition to halogens with the velocities for the two pure substances, and is based upon the observations of Sudborough and Thomas (J., 1910, **97**, 715, 2450) that halogens react additively much more rapidly at a $\beta\gamma$- than at an $\alpha\beta$-double bond. Notwithstanding the observations of Bougault (*loc. cit.*; *Ann. Chim.*, 1908, **15**, 296), it is doubtful whether halogens ever react completely at a $\beta\gamma$-double bond under conditions in which the $\alpha\beta$-isomeride is unchanged. It has therefore been necessary to measure the percentage reaction over a definite interval of time.

In general, the reacting substances are used in molecular quantities, the halogen being present in the form of a stable standardised solution. Other conditions, such as the nature and state of activation of the halogen, temperature, light, concentration, the nature of the solvent, and the presence of catalysts, may be varied to bring the reaction within the region of convenient experimental investigation; *e.g.*, in a given series the unsaturated acids will require

conditions more favourable to addition than will the corresponding, more positive ketones. The method has so far been used to determine the compositions of various mixtures of unsaturated acids. Preliminary work has been carried out on ketones and esters and it is hoped to communicate these results shortly.

### 1. *Examination of the Pure Acids.*

*Materials.*—The acids examined were: (1) *cyclo*Hexylideneacetic acid (Wallach, *Annalen*, 1909, **365**, 261), (2) $\Delta^1$-*cyclo*hexenylacetic acid (Kon and Speight, J., 1926, 2727; Farrow and Kon, *ibid.*, p. 2128), (3) ββ-diethylacrylic acid, (4) β-ethyl-$\Delta^\beta$-pentenoic acid, and (5) β-methyl-β-ethylacrylic acid, all three prepared by Kon and Linstead's method (*loc. cit.*), and (6) β-methyl-$\Delta^\beta$-pentenoic acid, which was made by boiling β-hydroxy-β-methylvaleric acid with 12½% sulphuric acid for 2½ hours and obtained, in 35% yield, almost free from its isomeride; it was purified by fractional distillation. The acids used in the analytical work had the following physical properties: (1) Plates, m. p. 90—91°, b. p. 159—160°/22 mm., from light petroleum; (2) plates, m. p. 36—38°, b. p. 152°/23 mm.; (3) b. p. 124°/13 mm., $[R_L]_D$ 36·59 (*p*-toluidide, m. p. 81°); (4) b. p. 112°/10 mm., $[R_L]_D$ 35·82 (*p*-toluidide, m. p. 94°); (5) flattened needles, m. p. 45°, b. p. 104°/13 mm., from light petroleum (*p*-toluidide, m. p. 67°); (6) b. p. 101°/14 mm., $[R_L]_D$ 31·07 (*p*-toluidide, m. p. 84°).

The halogen used was bromine, purified by the method of Sudborough and Thomas (*loc. cit.*). The solvents were carefully freed from traces of acid and were dried and fractionated twice before use.

*Reaction.*—The reaction was carried out under conditions differing from those of Sudborough and Thomas (*loc. cit.*) in several details (compare also Mills, J., 1883, **43**, 435). The solutions of the reagents were mixed in bulk instead of in aliquot portions. Immediately before readings were taken, quantities of 50 c.c. each were drawn into a pipette connected by a three-way tap with a low vacuum and were run, after definite intervals of time, into a solution of potassium iodide; the liberated iodine was titrated with *N*/20-thiosulphate. The other conditions observed were as follows:

*Solvent.* For acids (1) and (2), carbon tetrachloride; for acids (3), (4), (5), and (6), chloroform.

*Concentration.* 1/60 G.-mol. per litre (1/120 g.-mol. of the acid was dissolved in 250 c.c. of the inert solvent. The equivalent amount of bromine was obtained by making the necessary quantity of a freshly standardised solution of bromine up to 250 c.c.).

*Temperature.* 25°, controlled by a thermostat.

*Lighting.* All the reactions were carried out in blackened flasks.

*Results.*—The absorption of bromine is abnormally fast during the first 2 minutes of the reaction, but thereafter it pursues a bimolecular course and can easily be followed. As observed by previous workers, in general the readings do not give very concordant values for the velocity coefficient, $k = x/at(a - x)$, but there is no steady rise or fall indicating the occurrence of a secondary reaction.* The results are in Table I; the values of $a$ and $a - x$ are given by the number of c.c. of thiosulphate required at the beginning and the end of a period of $t$ hours. All the reaction velocities are derived from figures representing fractional changes and therefore are directly comparable (with the exception of those for the *cyclo*hexane acids, where a different solvent was used). The figures are thus independent of the strength of the thiosulphate solution, which was renewed and restandardised from time to time. Two of Sudborough and Thomas's results at 15°, marked * in the table, are given for comparison.

TABLE I.

*Unsaturated Acids + Bromine at* 25°.

| Acid. | Solvent. | $k$. Minimum. | $k$. Maximum. | $k$. Mean. | No. of readings |
|---|---|---|---|---|---|
| *cyclo*Hexylideneacetic ..... | $CCl_4$ | $0{\cdot}65\times10^{-2}$ | $2{\cdot}08\times10^{-2}$ | $1{\cdot}04\times10^{-2}$ | 6 |
| $\Delta^1$-*cyclo*Hexenylacetic ..... | ,, | 0·43 | 1·91 | 1·07 | 9 |
| ββ-Diethylacrylic ..... | $CHCl_3$ | $1{\cdot}17\times10^{-3}$ | $2{\cdot}28\times10^{-3}$ | $1{\cdot}91\times10^{-3}$ | 4 |
| β-Ethyl-$\Delta^\beta$-pentenoic ..... | ,, | $0{\cdot}74\times10^{-2}$ | $5{\cdot}67\times10^{-2}$ | $1{\cdot}15\times10^{-2}$ | 4 |
| β-Methyl-β-ethylacrylic ... | ,, | $0{\cdot}44\times10^{-3}$ | $3{\cdot}53\times10^{-3}$ | $2{\cdot}08\times10^{-3}$ | 3 |
| β-Methyl-$\Delta^\beta$-pentenoic ..... | ,, | $1{\cdot}35\times10^{-2}$ | $2{\cdot}75\times10^{-2}$ | $2{\cdot}03\times10^{-2}$ | 6 |
| β-Methyl-$\Delta^\alpha$-butenoic *..... | $CCl_4$ | $3{\cdot}1\times10^{-3}$ | $7{\cdot}3\times10^{-3}$ | — | — |
| $\Delta^\alpha$-Butenoic* ..... | ,, | $4{\cdot}68\times10^{-6}$ | $6{\cdot}16\times10^{-6}$ | — | — |

*Analysis of the Results.*—From the structural point of view several interesting points arise from these results. In the first place, the effect of conjugation in the αβ-acids is to give a velocity coefficient 1/10—1/100 of that found for the βγ-acid. Secondly, substitution of positive groups for hydrogen leads to an increased velocity of reaction, the *cyclo*hexane ring having an exceptionally great effect. Finally, the results for the addition of bromine to ββ-diethylacrylic acid and its $\Delta^\beta$-isomeride show that the latter (*p*-toluidide, m. p. 94°; amide, m. p. 114°) has the greater velocity of reaction and is therefore the βγ-acid—a result in agreement with the observations of Kon and Linstead (*loc. cit.*) on the structure of these acids.

### 2. *Examination of Mixtures of the Acids.*

*Materials.*—The investigation of mixtures of isomeric acids was carried out with mixtures obtained by the action of alkali on the pure acids under various conditions, and with artificial mixtures

* Hydrogen bromide is slowly liberated from the reaction product after some time, the change being facilitated by the presence of water.

of known compositions prepared by mixing together the pure isomerides.

The equilibration of the acids was carried out in the manner described in the following paper. With the exception of the *cyclo*hexyl acids, the resulting mixtures were distilled under reduced pressure, a fraction covering the boiling points of both isomerides being collected in each case. The absence of saturated impurity—*e.g.*, hydroxy-acids formed by the addition of water at the double bond—was proved by determinations of the total capacity of the mixtures for nascent bromine by Vaubel's method (*J. pr. Chem.*, 1893, **48**, 75) as modified by Callan and Russell Henderson (*J. Soc. Chem. Ind.*, 1922, **41**, 161T). In all the analyses made in this way, the titration figures agreed with those required for the addition of two atoms of bromine. The results are in Table II.

TABLE II.

*Acids + Nascent Bromine.*

| Series. | *cyclo*Hexyl. | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Initial material ..... | $\alpha\beta$ | $\beta\gamma$ | $\alpha\beta$ | $\alpha\beta$ | $\alpha\beta$ | $\beta\gamma$ | $\beta\gamma$ | $\beta\gamma$ |
| % Alkali used ..... | — | — | 60 | 50 | 40 | 60 | 50 | 40 |
| Br added (mg.). found ..... | 87·4 | 86·3 | 81·5 | 73·9 | 46·5 | 42·7 | 39·5 | 53·7 |
| Br added (mg.). calc.* ..... | 87·4 | 87·7 | 78·7 | 70·4 | 45·8 | 42·3 | 39·5 | 53·7 |

| Series. | $\beta$-Ethylpentenoic. | | | $\beta$-Methylpentenoic. | | |
|---|---|---|---|---|---|---|
| Initial material ..... | $\alpha\beta$ | $\beta\gamma$ | $\alpha\beta$ | $\alpha\beta$ | $\beta\gamma$ | $\alpha\beta$ |
| % Alkali used ..... | — | — | 60 | — | — | 60 |
| Br added (mg.). found ..... | 59·3 | 43·3 | 60·3 | 49·9 | 60·7 | 86·3 |
| Br added (mg.). calc.* ..... | 57·9 | 43·3 | 57·2 | 47·5 | 61·4 | 87·7 |

* Calculated for the addition of two atoms of bromine per molecule.

After proof of their purity had been obtained in this way, the mixtures of acids were examined by the bromine-addition method, the reactions being carried out exactly as with the pure acids.

*Analysis of Results.*—The mixtures of acids gave figures for the addition of bromine intermediate between those obtained for the parent substances. The velocity coefficients for the pure acids were not sufficiently accurate to allow of their use as constants in a mathematical analysis of the subject, and the compositions of the mixtures were therefore determined empirically by comparing the addition figures for the mixtures with those for mixtures prepared from definite quantities of the pure isomerides. This was most conveniently done in the manner indicated below.

The addition curves for the β-methylpentenoic acids (Fig. 1) show that at the end of the first 2 minutes the addition is proceeding comparatively slowly. Determinations made in this region are

therefore not liable to appreciable experimental error; moreover there is little danger of discrepancies arising from side reactions which may develop later, such as that due to the catalytic effect of hydrogen bromide liberated from the products of the reaction. The connexion between composition and addition is given in Table III, which shows the percentage addition of bromine in 2 minutes to various mixtures of acids of known composition.

FIG. 1.

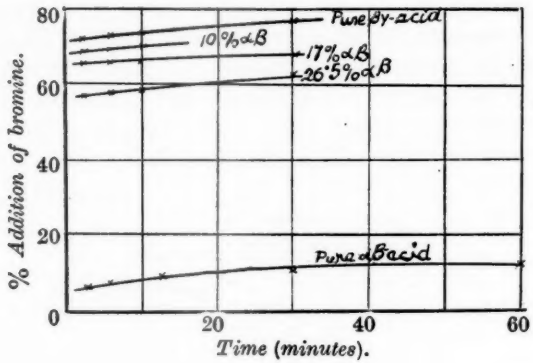



TABLE III.

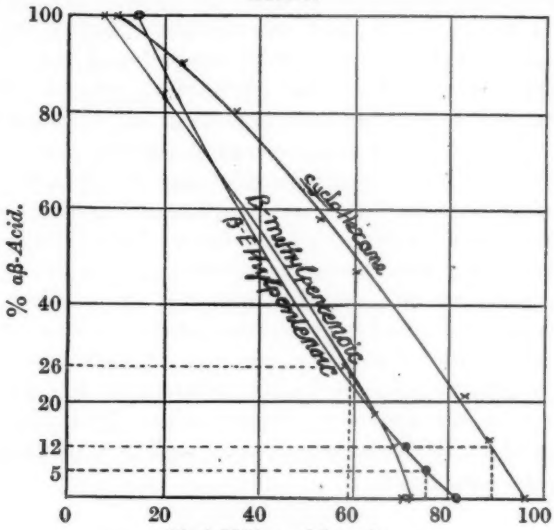
| Comp. of acid. % αβ. | Comp. of acid. % βγ. | Addition. %. |
|---|---|---|
| *cyclo*Hexane series. | | |
| 0 | 100 | 95·6 |
| 14·3 | 85·7 | 88·1 |
| 20·9 | 79·3 | 84·0 |
| 46·0 | 54·0 | 59·9 |
| 58·0 | 42·0 | 54·3 |
| 79·7 | 20·3 | 34·7 |
| 90·1 | 9·9 | 24·0 |
| 100 | 0 | 10·4 |
| β-Ethylpentenoic series. | | |
| 0 | 100 | 81·3 |
| 5·1 | 94·9 | 74·5 |
| 8·2 | 91·8 | 70·0 |
| 100 | 0 | 15·0 |
| β-Methylpentenoic series. | | |
| 0 | 100 | 70·2 |
| 10·1 | 89·9 | 67·9 |
| 17·0 | 83·0 | 64·2 |
| 26·5 | 73·5 | 57·6 |
| 100 | 0 | 7·2 |

It will be seen that the amount of addition is roughly proportional to the percentage of βγ-acid. The variation from this relationship is shown in Fig. 2, where the two-minute addition figures for the three series are plotted against composition. The complete curve has been obtained only for the *cyclo*hexane acids; in the other series, only mixtures in the neighbourhood of the equilibrium point were examined.

The compositions of the various mixtures of acids obtained on equilibration were readily determined from the addition values and reference to the appropriate curves. The positions of the

equilibrium mixtures are shown by the dotted lines in Fig. 2, and the addition values and the compositions calculated from them are in Table IV.

FIG. 2.




*Dotted lines represent equilibrium mixtures.*

TABLE IV.

*Addition Values and Compositions of Equilibrium Mixtures.*

| Series. | Initial acid. | % Alkali. | Time (hrs.). | % Addition of bromine (2-min.). | % αβ-Acid in mixture. |
|---|---|---|---|---|---|
| *cyclo*Hexane | αβ | 60 | 1·0 | 87·9 | 13 |
| | αβ | 60 | 24·0 | 89·4 | 11 |
| | αβ | 50 | 1·55 | 87·8 | 13 |
| | αβ | 50 | 24·0 | 89·08 | 11 |
| | αβ | 40 | 24·0 | 87·8 | 13 |
| | βγ | 60 | 23·0 | 89·4 | 11 |
| | βγ | 50 | 24·0 | 87·8 | 13 |
| | βγ | 40 | 24·0 | 87·8 | 13 |
| β-Ethylpentenoic | αβ | 60 | 0·33 | 76·4 | 4 |
| | αβ | 60 | 0·33 | 74·1 | 5 |
| | βγ | 60 | 0·5 | 73·5 | 6 |
| β-Methylpentenoic | αβ | 60 | 0·33 | 58·3 | 26 |
| | βγ | 60 | 0·25 | 58·5 | 26 |

The positions of equilibrium between the pairs of acids in boiling potassium hydroxide solution * are therefore :

| | | |
|---|---|---|
| *cyclo*Hexane acids | 12·0 ± 0·8% αβ | 88 ∓ 0·8% βγ |
| β-Ethylpentenoic acids | 5% αβ | 95% βγ |
| β-Methylpentenoic acids | 26% αβ | 74% βγ |

* The effect of alterations in the conditions on the position of equilibrium will be discussed in a future paper.

These are genuine equilibria in that they can be reached from either side and are unchanged by further action. Beesley, Ingold, and Thorpe (J., 1915, **107**, 1081), who first observed the change of *cyclo*hexylideneacetic acid into $\Delta^1$-*cyclo*hexenylacetic acid, described it as complete and irreversible. That statement is, however, easily explained when it is remembered that the *cyclo*hexenyl acid separates from the equilibrium mixture in a solid form and, on the small scale on which those investigators worked, the 12% of αβ-acid might easily escape detection. As a result of the earlier work on the equilibration of the substituted pentenoic acids, Kon and Linstead (*loc. cit.*) stated that, whereas in the β-ethyl series the conversion of the αβ- into the βγ-form was apparently complete, in the β-methyl series the equilibrium was further on the side of the αβ-acid, although the βγ- still preponderated. The figures now obtained confirm this earlier work in all respects.

A curious feature of the present work is that equilibrium is reached in about 20 minutes in the substituted pentenoic acids, but only in an hour in the *cyclo*hexane acids. Thus the aliphatic acids appear to be the more mobile, although in the corresponding ketones the reverse is true.

The author wishes to thank Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in the progress of this research. His thanks are also due to the Government Grant Committee of the Royal Society for a grant which has largely defrayed its cost.

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## LVI.—*The Chemistry of the Three-carbon System. Part XI. The Mechanism of Isomeric Change in Unsaturated Acids.*

By REGINALD PATRICK LINSTEAD.

TAUTOMERIC compounds with retarded mobility may be regarded from the structural standpoint as insufficiently activated for complete mobility, or from the kinetic standpoint their inertia may be attributed to the infinitesimal velocities of the interconversion reactions under ordinary conditions. In such compounds, isomeric change can occur only in the presence of more or less powerful

reagents, and it is this peculiarity which has led to some doubt being cast on the genuineness of the tautomerism exhibited by them. It is held that such changes can be accounted for by the addition and splitting off of the catalyst. Support is given to these views by the production, side by side with the isomeric changes, of addition compounds which could function as such intermediates. Thus Butlerov (*Annalen*, 1877, **189**, 44) and Fittig (*ibid.*, 1894, **283**, 47) have observed the addition of water during changes in unsaturated hydrocarbons and acids, and Farmer that of methyl alcohol in the dihydromuconic esters (J., 1923, **123**, 3324). The ease with which a base may function in this way is shown by the work of Ruhemann (J., 1898, **73**, 723), who observed the readiness with which these substances can be added to unsaturated systems. Only in one example has it been shown that the addition product actually formed is not that which could act as a catalyst (Ingold, Shoppee, and Thorpe, J., 1926, 1477).

The interconversion of unsaturated acids in the presence of alkali furnishes a good example of retarded isomeric changes for the explanation of which two mechanisms can be suggested: (A) the β-hydroxy-acid functions as an intermediate product and the change proceeds by the addition and splitting off of water, or (B) tautomeric change occurs between the αβ- and the βγ-unsaturated acid, and at the same time water can be added to the αβ-acid to give the β-hydroxy-acid, the process being reversible. Fittig

(A) $>CH\cdot C::C\cdot CO_2H \rightleftharpoons >CH\cdot \underset{HO}{C}-\underset{H}{C}\cdot CO_2H \rightleftharpoons >C::C\cdot CH\cdot CO_2H$

(B) $>CH\cdot \underset{HO}{C}-\underset{H}{C}\cdot CO_2H \rightleftharpoons >CH\cdot C::C\cdot CO_2H \rightleftharpoons >C::C\cdot CH\cdot CO_2H$

(*loc. cit.*), who first observed the change and the simultaneous formation of the β-hydroxy-acid, was unable to decide between these mechanisms, and with the exception of Knoevenagel's application of the Thiele hypothesis to the change (*Annalen*, 1900, **311**, 217) little further work appears to have been done either on the clearing up of this point or on the reaction as a whole.

If the tautomeric explanation (B) is correct, evidence in its favour will be forthcoming only when the additive reaction is very slow in comparison with the direct isomeric change. For example, if interconversion can be shown to occur under conditions which preclude the possibility of the presence of the β-hydroxy-acid, or the possibility of its dehydration is present, the tautomeric hypo-

thesis will receive strong support. In some of the work of Fittig (*Annalen*, 1894, **283**, 68, 132, 297), examples of acids can be found which cast doubt on the water-addition hypothesis. Thus the pentenoic and *iso*heptenoic acids undergo interconversion under conditions in which the β-hydroxy-acid is comparatively stable, whilst in the γ-phenylbutenoic acids the conversion of the βγ- into the αβ-form stops at a definite point and further action of alkali causes an increased addition of water without affecting this equilibrium (compare Linstead and Williams, J., 1926, 2736).

The interconversion of $\Delta^1$-*cyclo*hexenylacetic acid and *cyclo*hexylideneacetic acid now to be described is particularly suitable for investigation, as both the unsaturated acids and the corresponding β-hydroxy-acid, *cyclo*hexanolacetic acid, $C_5H_{10}{>}C(OH)\cdot CH_2\cdot CO_2H$, are easily prepared and are crystalline, and the addition of water to the unsaturated system is extremely slow, the condition given above thus being satisfied.

Whilst the βγ- is the more stable form, the αβ- has considerable stability; *e.g.*, the sodium salt of the αβ-acid resists interconversion in neutral solvents even at high temperatures, and the acid itself is unaffected by sodium bicarbonate and piperidine. It is only in the presence of hot alkali hydroxides that movement of the bond can occur.

The study of the action of alkalis on the three acids is complicated by the fact that the β-hydroxy-acid readily undergoes hydrolytic fission in the presence of boiling potassium hydroxide solution with the formation of *cyclo*hexanone and potassium acetate: $C_5H_{10}{>}C(OH)\cdot CH_2\cdot CO_2H \longrightarrow C_5H_{10}{>}CO + CH_3\cdot CO_2K$. The unsaturated acids yield these products only after more prolonged boiling with alkali, and it may therefore be supposed that addition of water to them precedes fission. The results resemble those obtained by Farrow and Kon (J., 1926, 2131) for some related unsaturated ketones.

The reactions were examined quantitatively under various conditions by the methods given on p. 369. After the requisite time of reaction, the product was divided in the usual way into a neutral fraction, containing the *cyclo*hexanone, and an acid fraction, containing any or all of the four possible acids. The acetic acid was readily separated owing to its volatility, and the *cyclo*hexanolacetic acid by its insolubility in light petroleum, in which the unsaturated acids are soluble. The unsaturated acids were estimated by the bromine addition method (preceding paper). The results are in Table I.

Some of the interconversion results obtained with the unsaturated

## TABLE I.

*Action of potassium hydroxide solution on* cyclo*hexanolacetic acid.*

| | | | Composition of product (as % of initial material). | | | | |
|---|---|---|---|---|---|---|---|
| % KOH. | Time (hrs.). | Temp. | Unchanged acid. | Unsaturated acid.* | *cyclo*-Hexanone. | Acetic acid. | % Loss. |
| 1 | 48 | b. p. | 84·6 | 2·5 | 0 | 0 | 12·9 |
| ,, | 100 | ,, | 86·8 | 1·1 | ,, | ,, | 12·1 |
| 10 | 1 | ,, | 92·0 | 4·3 | ,, | ,, | 3·7 |
| ,, | 24 | ,, | 85·2 | 2·7 | trace | ,, | 12·1 |
| 60 | 24 | 20° | 83·4 | 8·4 | 0 | ,, | 8·2 |
| ,, | 1 | b. p. | 72·1 | 9·0 | 10·1; 11·3 | — | 8·8 |
| ,, | 1·5 | ,, | 22·9 | 18·1 | 25·6 | 9·0 | 33·4 |
| ,, | 48 | ,, | 20·0 † | | 36·4 | 25·6 | 43·6 |

* Total figure; proportion of components not estimated.

† Not separated.

## TABLE II.

*Action of potassium hydroxide on unsaturated acids.*

(i) On *cyclo*hexylideneacetic acid.

| Expt. No. | % KOH. | Time (hrs.). | Temp. | Composition of product (% initial material). $\alpha\beta$-Acid. | $\beta\gamma$-Acid. | % Loss. |
|---|---|---|---|---|---|---|
| 1 | 1 | 24 | 20° | 98·8 | 0 | 1·2 |
| 2 | 10 | 24 | ,, | 96·8 | 0 | 3·2 |
| 3 | ,, | 1 | b. p. | 94·0 | 0 | 6·0 |
| 4 | ,, | 24 | ,, | 82·2 | 16·8 | 1·0 |
| 5 | 20 | 1 | ,, | 94·8 | 2·9 | 2·3 |
| 6 | 30 | 1 | ,, | 81·8 | 14·4 | 3·8 |
| 7 | 40 | 0·25 | ,, | 93·3 | 6·4 | 0·3 |
| 8 | ,, | 1 | ,, | 55·3 | 28·5 | 16·2 |
| 9 | ,, | 24 | ,, | 12·5 | 83·3 | 4·2 |
| 10 | 50 | 0·5 | ,, | 61·5 | 31·7 | 6·8 |
| 11 | ,, | 1 | ,, | 23·5 | 70·5 | 6·0 |
| 12 | ,, | 1·55 | ,, | 12·7 | 84·9 | 2·4 |
| 13 | ,, | 24 | ,, | 10·5 | 84·5 | 5·0 |
| 14 | 60 | 0·25 | ,, | 74·5 | 22·7 | 2·8 |
| 15 | ,, | 0·5 | ,, | 19·9 | 58·1 | 22·0 |
| 16 | ,, | 0·83 | ,, | 15·7 | 76·7 | 7·6 |
| 17 | ,, | 1 | ,, | 12·5 | 83·5 | 4·0 |
| 18 | ,, | 24 | ,, | 8·0 | 64·4 | 25·2 |
| | | | (ii) On $\Delta^1$-*cyclo*hexenylacetic acid. | | | |
| 19 | 10 | 1 | b. p. | 0 | 94·2 | 5·8 |
| 20 | 40 | 1 | ,, | 0 | 90·6 | 9·4 |
| 21 | ,, | 24 | ,, | 12·2 | 81·4 | 6·4 |
| 22 | 50 | 1 | ,, | 7·8 | 78·2 | 14·2 * |
| 23 | ,, | 24 | ,, | 12·4 | 82·6 | 5·0 |
| 24 | 60 | 1 | ,, | 7·0 | 63·4 | 29·6 * |
| 25 | ,, | 23 | ,, | 7·9 | 63·9 | 26·3 * |

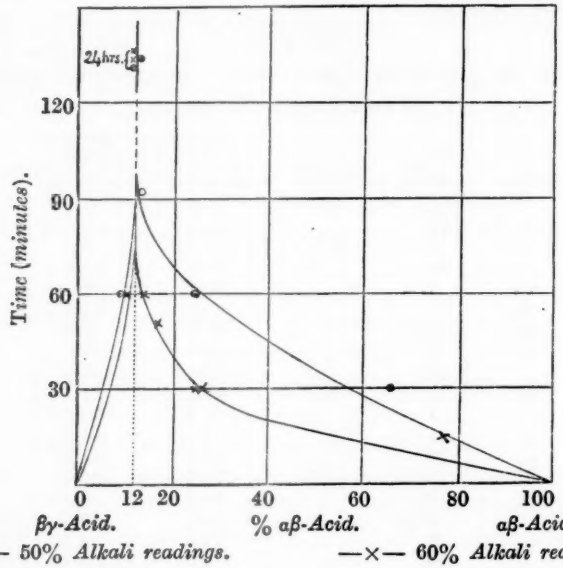
In experiment 18, the product also contained a trace of the $\beta$-hydroxy-acid, 2·6% of *cyclo*hexanone, and 1·6% of acetic acid. In experiment 25, the quantities of the same three products were a trace, 0·4%, and 2·9%, respectively. Traces of the $\beta$-hydroxy-acid were detected in experiments 22 and 24.

* Acid product distilled.

acids are given graphically in Fig. 1, where the percentage of αβ-acid in the mixture is plotted against time. The asymptotic approach to equilibrium is clearly shown.

The first point of interest that emerges from the results is the small loss which is experienced throughout, except where a large amount of fission has occurred, and in those experiments where the acid product was distilled under reduced pressure. This ensures the trustworthiness of the results as a whole. In the experiments on the unsaturated acids, no addition of water occurred, the absence of hydroxy-acid being proved in all cases by the nascent bromine method (see preceding paper). The slow rate of hydration is

FIG. 1.




clearly shown by the results of some of the experiments with 60% alkali acting for 23 or 24 hours, where 36% of fission takes place from the hydroxy-acid, but only 2—3% when the unsaturated acids are used. This may possibly be due to the slowness with which the negative hydroxyl ion is added to the ion of the dissociated salt of the acid (compare Higginbotham and Lapworth, J., 1922, **121**, 49). The steric effect of the *cyclo*hexane ring also may inhibit addition. The absence of β-hydroxy-acid from the final product cannot in itself be taken as a proof that the acid does not intervene in the isomerisation, but it is clear from some of the above results that if it were formed it could not be dehydrated in quantity sufficient to account for the rapid interconversion of the unsaturated

acids. Thus the 1-hour readings with 60% alkali show that 84% of interconversion occurs under conditions in which only 9% of hydroxy-acid is dehydrated, and the 24-hour readings with 10% alkali show that 17% of interconversion occurs where the β-hydroxy-acid is almost completely unaffected.

Under ideal conditions, the interconversion reaction should be unimolecular if it is due to tautomerism and bimolecular if dependent on the addition and splitting off of water. In an infinite excess of water, however, the rate of interconversion would depend only on the concentration of the acid, whichever mechanism were true. Experimental evidence on this point, therefore, can hardly be conclusive, for a considerable excess of water was present, even in the 60% alkali experiments, where the molecular proportions of acid, potassium hydroxide, and water were 1 : 10 : 20·7.

The kinetics of unimolecular reversible reactions have been investigated by Küster (*Z. physikal. Chem.*, 1895, **18**, 171) and by Lowry (J., 1899, **75**, 224), and the equation proposed by Küster has been successfully applied to tautomeric equilibria. This connects the change in concentration of the substance, A, initially present ($x$) with the time ($t$) by the expression

$$t(k_1 + k_2) = \log_e \{\xi/(\xi - x)\} \quad . \quad . \quad . \quad . \quad (1)$$

where $\xi$ is the value of $x$ at equilibrium and $k_1$ and $k_2$ are the velocity coefficients of the forward and the back reaction respectively. The values of $k_1$ and $k_2$ can then be found from the equilibrium values for the concentration of A :

$$K = k_1/k_2 = \xi/(a - \xi) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $a$ is the initial concentration of A.

The equilibrium in the pair of acids now under discussion being taken as 12% αβ-acid $\rightleftharpoons$ 88% βγ-acid (see preceding paper), the application of the Küster equation gives the results in Table III.

TABLE III.

60% Alkali (ten times the quantity required for neutralisation).

Concentrations in g./c.c. Time in minutes.

| A. | $t$. | $x$. | $\xi - x$. | $k_1 + k_2$. |
|---|---|---|---|---|
| αβ-Acid | 15 | 0·0865 | 0·2444 | (0·020) |
| ,, | 30 | 0·2801 | 0·0508 | 0·062 |
| ,, | 50 | 0·3121 | 0·0188 | 0·057 |
| ,, | 60 | 0·3271 | 0·0038 | 0·075 |
| βγ-Acid | 60 | 0·0376 | 0·0075 | 0·068 |
| 50% Alkali (ten times the quantity required for neutralisation). | | | | |
| αβ-Acid | 30 | 0·0850 | 0·1351 | (0·016) |
| ,, | 60 | 0·1875 | 0·0326 | 0·032 |
| ,, | 93 | 0·2150 | 0·0051 | 0·040 |

When the severe conditions and the powerful nature of the catalyst are taken into consideration, the agreement between the figures for the constants must be regarded as good.

The individual values of $k_1$ and $k_2$ can be calculated from equation (2), the mean values for $k_1 + k_2$, 0·066 (60% alkali) and 0·036 (50% alkali), and the known value, 88 : 12, for the ratio of the quantities of the acids at equilibrium, being used. These are :

| % Alkali | 60% | 50% |
|---|---|---|
| $k_1(\alpha\beta \longrightarrow \beta\gamma)$ | 0·058 | 0·032 |
| $k_2(\beta\gamma \longrightarrow \alpha\beta)$ | 0·008 | 0·004 |

These figures furnish the first quantitative values for the mobility of a system of this type under specified conditions. Comparison between them and similar figures for other series would be of real significance in the study, *e.g.*, of the effect of positive groups on mobility. For such a purpose the conditions of the equilibration would have to be standardised—those used in the present work would be unsuitable because (1) the concentrations of the reagents are so high that in many series dissolution of the potassium salt would probably be incomplete, and the presence of a solid phase would affect the determinations of reaction velocity (the potassium salts of the two *cyclo*hexane acids are only just dissolved by the boiling 60% alkali solution); (2) the unstable acids might decompose at the high reaction temperature; (3) the change in the *cyclo*hexane series is comparatively slow (see preceding paper). In a very mobile series the change might proceed at a rate too fast for experimental measurement, under the conditions which produce complete equilibration in some 65 minutes in the present series.

By decreasing the concentrations of the reactants and reducing the severity of the reaction, it is hoped to arrive at a standard set of conditions capable of general use.

*The Effect of Conditions on Interconversion.*

The experimental results show that the rate of isomeric change depends on the concentration of alkali. This may function in two ways. In the first place, increase in alkali concentration decreases the amount of water and increases the concentration of the potassium salt of the acid. Secondly, the experiments are carried out at the boiling point of the solution, and this rises with increasing concentration, the 60% solution boiling at about 145°. The experimental figures available do not at present allow of a distinction being made between the temperature and the concentration effects.

The concentration of alkali does not appear to have any effect

on the ultimate position of equilibrium, as there is close agreement between the results obtained with 40, 50, and 60% alkali (compare preceding paper). Johnson and Kon (J., 1926, 2748) reached the same conclusion in their investigation on the movement of the double bond in substituted cinnamic acids. From the theoretical standpoint this is unexpected, as change in temperature should displace the equilibrium in all systems except those in which the heat of reaction is zero for the tautomeric change. Küster (*loc. cit.*) showed that the position of equilibrium between the isomeric keto-pentachloro*cyclo*pentenes was considerably affected by temperature. A more accurate experimental method for the study of these and similar isomeric changes at constant temperature has now been devised and the influence of temperature on these reactions is being studied.

### *The Mechanism of the Reaction.*

The experimental results already described provide strong support for the tautomeric nature of the reaction, but the inner mechanism of such a change is not yet clear. It can be interpreted on the lines suggested by Ingold, Shoppee, and Thorpe's application of Robinson's theory (*loc. cit.*) as an example of a highly polar catalyst facilitating the removal of the mobile hydrogen atom from the system in the form of a proton. This new hypothesis, whilst accounting for many of the experimental facts, would appear to disregard the close connexion between the enolising power of activating groups and mobility (compare Farrow and Kon, J., 1926, 2128).

## EXPERIMENTAL.

*Materials.*—The acids used were prepared by the methods given in the preceding paper, and had the properties recorded there. *cyclo*Hexanolacetic acid was prepared by Wallach's method (*Annalen*, 1906, **347**, 329); it crystallised from hot petroleum (b. p. 60—80°) in laminæ, m. p. 64°.

*Reaction with Alkali.*—The acid (5 g.) was added to a hot solution of potassium hydroxide (ten times the quantity required for neutralisation) in the requisite amount of water. Except in the experiments of very short duration, a copper reaction vessel was used, fitted with a double-surface condenser and with a soda-lime tube to eliminate carbon dioxide. The time of reaction was taken from the commencement of boiling, and at its conclusion the reaction vessel was plunged into ice and the contents were extracted with ether. The *cyclo*hexanone in the dried ethereal extract was slowly freed from solvent under a long column and was weighed and identi-

fied by conversion into its semicarbazone. The alkaline liquid was acidified, cooled, and extracted with an equal volume of ether divided in several portions, the ether being subsequently removed from the dried solution through a column. If the residue contained acetic acid, this was distilled off and estimated by titration with standard alkali. The residual acid was freed from the last traces of solvent in a good vacuum. In the experiments on *cyclo*hexanol-acetic acid, the unchanged acid invariably crystallised and was freed from unsaturated acid by washing it with petroleum (b. p. 40—60°). The insoluble acid which remained melted sharply, in all cases between 56 and 64°, and was identified by mixed melting-point determinations. The soluble, unsaturated acid was freed from solvent and weighed. The amount usually obtained was insufficient for a determination of the proportion of the isomerides. When the initial material was an unsaturated acid, the acid product was tested for hydroxy-acid by the nascent bromine method and was then examined by the bromine addition method (see preceding paper). The conditions used were: concentration, 1/60 g.-mol. per litre; solvent, carbon tetrachloride; temperature, 25°. The compositions of the mixtures were found by reference to the standard curves. In some of the earlier experiments, the product was distilled under reduced pressure before examination, but this resulted in loss and served no useful purpose.

The results of these observations are in Tables I and II. The accuracy of the methods of extraction and estimation was checked by blank experiments; *e.g.*, under the conditions used, 85% of the *cyclo*hexanone was recovered and the figures given in the tables are therefore the experimental figures multiplied by a factor (1·2). Similarly, 95% of the hydroxy-acid can be isolated by the petroleum separation method mentioned above, giving a factor of 1·05, which has been used in compiling the tables. One of the analyses of the mixed unsaturated acids was kindly checked by Mr. C. J. May by Bougault's method; the results are given below.

| | % $\beta\gamma$-Acid found. | % $\alpha\beta$-Acid found. | % Loss. |
|---|---|---|---|
| By bromine method ..... | 81·8 | 14·4 | 3·8 |
| By Bougault's method ..... | 77·9 | 18·3 | 3·8 |

The quantitative separation of mixtures of the unsaturated acids and of several of their salts by fractional crystallisation from a variety of solvents was attempted, but no process was discovered of sufficient accuracy to check the figures obtained by the bromine method.

*Sodium* cyclo*hexylideneacetate* was prepared in theoretical yield by the action of " molecular " sodium on the acid in benzene solution. The gelatinous product was washed with ether and dried.

The pure salt forms fine, white needles, m. p. 276° (decomp.), from ethyl alcohol (Found : Na, 13·9. $C_8H_{11}O_2Na$ requires Na, 14·2%). It is insoluble in most organic solvents, soluble in water, and very soluble in methyl alcohol.

The pure salt was unaffected after being boiled with xylene, alcohol or water for 24 hours; pure *cyclo*hexylideneacetic acid was obtained on acidification.

The author's thanks are due to Professor J. F. Thorpe, F.R.S., and Dr. G. A. R. Kon for their interest in the progress of this research, and to the Royal Society for a grant which has largely defrayed its cost.

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## LVII.—iso*Erucic Acid.*

By TAHILRAM JETHANAND MIRCHANDANI and JOHN LIONEL SIMONSEN.

*iso*ERUCIC acid was first obtained by Alexandrov and Saytzev (*J. pr. Chem.*, 1894, **49**, 58) by treating iodobehenic acid, prepared from erucic acid, with potassium hydroxide. Saytzev (*ibid.*, 1894, **50**, 65) showed that it also resulted when brassidic acid was converted into iodobehenic acid and the halogen acid treated with alkali. *iso*Erucic acid, m. p. 54—56°, was characterised by the preparation of a dibromobehenic acid, m. p. 44—46°, and by oxidation in alkaline solution with potassium permanganate to a dihydroxybehenic acid, m. p. 86—88°. At the time of these investigations, erucic acid was considered to have the constitution (I), and the above-mentioned authors regarded it as probable that *iso*erucic acid was the structural isomeride (II).

(I.) $CH_3 \cdot [CH_2]_{17} \cdot CH{:}CH \cdot CH_2 \cdot CO_2H$ $CH_3 \cdot [CH_2]_{18} \cdot CH{:}CH \cdot CO_2H$ (II.)

(III.) $CH_3 \cdot [CH_2]_7 \cdot CH{:}CH \cdot [CH_2]_{11} \cdot CO_2H$

It was subsequently established that erucic acid and brassidic acid were the *cis*- and *trans*-modifications respectively of an acid (III), since on oxidation with ozone, followed by chromic acid, they both yielded brassylic and pelargonic acids (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1074; Jegorov, *J. pr. Chem.*, 1912, **86**, 539). The view of Alexandrov and Saytzev (*loc. cit.*) being accepted, it followed that *iso*erucic acid would in all probability

have either formula (VI) or (VII), depending on whether iodobehenic acid from erucic and brassidic acids had formula (IV) or (V).

(IV.) $CH_3 \cdot [CH_2]_6 \cdot CH_2 \cdot CHI \cdot [CH_2]_{12} \cdot CO_2H$

(V.) $CH_3 \cdot [CH_2]_8 \cdot CHI \cdot CH_2 \cdot [CH_2]_{10} \cdot CO_2H$

(VI.) $CH_3 \cdot [CH_2]_6 \cdot CH{:}CH \cdot [CH_2]_{12} \cdot CO_2H$

(VII.) $CH_3 \cdot [CH_2]_8 \cdot CH{:}CH \cdot [CH_2]_{10} \cdot CO_2H$

It was shown, however, by Ponzio (*Gazzetta*, 1904, **34**, ii, 50) that when *iso*erucic acid was oxidised by concentrated nitric acid, in a manner similar to that used in the oxidation of erucic acid (*J. pr. Chem.*, 1893, **48**, 323), it gave a mixture of acids from which brassylic and pelargonic acids were isolated and he showed further that the dibromo-acid (m. p. 44—46°), on treatment with alkali, yielded a behenolic acid identical with that obtained under the same conditions from the dibromo-acids derived from erucic and brassidic acids. As a result of these experiments he very legitimately concluded that *iso*erucic acid was not a structural isomeride of erucic and brassidic acids. In subsequent years, a number of investigations were carried out with the object of determining by physico-chemical methods the relationship of these three acids (Mascarelli and Toschi, *Gazzetta*, 1915, **45**, i, 314; Mascarelli and Sanna, *ibid.*, 1915, **45**, ii, 208, 315; Mascarelli, *ibid.*, 1917, **47**, i, 160). The conclusion was reached that in all probability brassidic and *iso*erucic acids were dimorphic forms of the *trans*-acid (III), but all attempts to convert one acid into the other failed.

Notwithstanding Ponzio's experiments, it appeared to us possible that the original view of Alexandrov and Saytzev might be correct, since the oxidation of an unsaturated fatty acid with concentrated nitric acid, owing to the extreme violence with which it proceeds, cannot be regarded as an entirely satisfactory method of orienting a double linking, whilst the conversion of the dibromobehenic acid into the acetylenic acid is carried out under conditions which are recognised as favourable to isomeric change.

Repetition of the oxidation of *iso*erucic acid with nitric acid has confirmed the formation of brassylic acid as one of the products of the reaction, but the yield of this dibasic acid is extremely small, the main substances formed being acids of lower molecular weight. We decided, therefore, to oxidise *iso*erucic acid, in the form of its ester, with ozone and also with potassium permanganate under the standard conditions used by Armstrong and Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 43 T) for the oxidation of methyl oleate.

The *iso*erucic acid used in these experiments was prepared by the method of Alexandrov and Saytzev (*loc. cit.*) and purified by

repeated crystallisation from alcohol (95%). It melted sharply at 55—57° and appeared to be homogeneous. Treatment of the *ethyl* ester with ozone gave, in addition to the main oxidation products, which will be discussed later, a not inconsiderable quantity of ethyl arachidate. There is no doubt that the *iso*erucic acid used in the earlier experiments was contaminated with arachidic acid, although the acid had the correct m. p. and crystallised extremely well. In our later experiments, the *iso*erucic acid, after crystallisation from alcohol to constant melting point, was further purified by fractional precipitation of the zinc salt, and any arachidic acid was thus removed in the least soluble fractions.

When ethyl *iso*erucate was oxidised with ozone, under conditions which, with erucic acid, were found to yield a readily separable mixture of brassylic and pelargonic acids (see p. 376), the oxidation product was a mixture which was somewhat difficult to resolve. As the quantity of this material was limited, we examined only the mixture of dibasic acids formed. We were able to isolate (*a*) decane-$\alpha\kappa$-dicarboxylic acid, $HO_2C{\cdot}[CH_2]_{10}{\cdot}CO_2H$, m. p. 126—127°, identified by comparison with a synthetic specimen of the acid (Walker and Lumsden, J., 1901, **79**, 1201), and (*b*) dodecane-$\alpha\mu$-dicarboxylic acid, $HO_2C{\cdot}[CH_2]_{12}{\cdot}CO_2H$, m. p. 121—122°, identified by analysis and by preparation of the methyl ester, m. p. 41°.

This result of the oxidation of ethyl *iso*erucate with ozone was surprising, and appeared to show that *iso*erucic acid, in spite of its sharp m. p. and well-defined crystalline form, was not homogeneous but was a mixture of the two unsaturated acids (VI) and (VII).

To confirm this conclusion, a quantity of very carefully purified methyl *iso*erucate was oxidised in acetone solution with potassium permanganate. From the oxidation products we were able to separate the two dibasic acids mentioned above and also *n*-octoic acid. Unfortunately, *n*-decoic acid, which must also have been formed, could not be obtained in a pure state.

This experiment confirmed in all respects the results obtained by oxidation with ozone and seems to leave no doubt that *iso*erucic acid is not a homogeneous substance, but is a mixture of $\Delta^{11}$-*docosene*-1-*carboxylic acid* and $\Delta^{13}$-*docosene*-1-*carboxylic acid*. From the yields of the oxidation acids the two acids would appear to be present in approximately equal amounts.

Since *iso*erucic acid itself was an inseparable mixture, we examined a number of derivatives to see whether any of them showed signs of heterogeneity. The *methyl* ester is crystalline, m. p. 24—26°, resolidifying at 22°; the *anilide* and p-*toluidide* both crystallise extremely well and both before and after crystallisation have the same m. p.; the *zinc* salt appears to be homogeneous.

As has already been mentioned, *iso*erucic acid is stated to yield a dibromo-derivative, m. p. 42—44°, or 46—46·6° according to Macbeth and Stewart (P., 1912, **28**, 68). We have repeated the preparation of this substance several times, but in every case the bromination product had the appearance of a mixture and the m. p. was not sharp. We have not tried the oxidation of *iso*erucic acid to dihydroxybehenic acid, but it is probable that this is a mixture of two dihydroxy-acids.

The fact that *iso*erucic acid is an inseparable mixture of two acids yielding apparently homogeneous derivatives is somewhat unusual, but is not unique. Attention may be directed to the following somewhat similar cases: mononitro-*o*-veratraldehyde, m. p. 88° (Perkin, Roberts, and Robinson, J., 1914, **105**, 2389), has been shown to be a mixture of two isomeric nitroveratraldehydes of m. p. 110° and 113° respectively (Perkin, Robinson, and Stoyle, J., 1924, **125**, 2355); anisic and veratric acids form a mixture, m. p. 145°, inseparable by crystallisation (Cain and Simonsen, J., 1912, **101**, 1061); the geometrical isomerides of camphorquinone-oxime (*iso*nitrosocamphor) are inseparable by solvents and produce a mixture melting higher than the more fusible modification (Forster, J., 1903, **83**, 535); benzoic and *p*-nitrobenzoic acids in the proportion 2 : 1 form a mixture indivisible by solvents and melting at 182—198° (Forster and Saville, J., 1922, **121**, 823).

During our preliminary experiments we investigated the oxidation of erucic and brassidic acids under various conditions and found the nature of the dihydroxy-acid formed to be dependent on the conditions used. In view of the recent publication of Hilditch (J., 1926, 1828) we do not intend to continue this side of the investigation. Experiments on the synthesis of the two unsaturated acids (VI and VII) are in progress and will, it is hoped, form the subject of a future communication.

## EXPERIMENTAL.

*iso*Erucic acid prepared by Alexandrov and Saytzev's method (*loc. cit.*), after four crystallisations from alcohol, melted at 54—56°, but, as has already been mentioned, it was found as the result of oxidation experiments to contain a small percentage of arachidic acid. The acid was purified by fractional precipitation of the zinc salt; eight fractions were obtained, of which the first two were rejected, since they contained arachidic acid. After this purification, the acid had m. p. 55—57° and $n_D^{64^\circ}$ 1·4469.*

*iso*Erucic acid is not affected by treatment with nitrous acid under conditions which convert erucic acid into brassidic acid, nor does it

* The refractive indices of erucic and brassidic acids at the same temperature were 1·4480 and 1·4472, respectively.

undergo any change when an alcoholic solution containing a trace of iodine is exposed to bright sunlight for some days.

The *zinc* salt crystallised from benzene in thin leaflets, m. p. 109°. No depression of the m. p. occurs on admixture with an equal amount of the zinc salt of brassidic acid (m. p. 112—113°), but the crystalline forms of the two salts are different, the latter salt crystallising in needles.

The *anilide* separated from alcohol in fine needles, m. p. 77—78·5° (Found : N, 3·6. $C_{28}H_{47}ON$ requires N, 3·4%), and the p-*toluidide* in needles, m. p. 85—86° (Found : N, 3·5. $C_{29}H_{49}ON$ requires N, 3·3%).

The *methyl* ester, prepared by treating the acid with methyl alcohol and sulphuric acid, crystallised in needles, b. p. 240°/14 mm., m. p. about 24—26°, resolidifying at 22° (thermometer in liquid). It is somewhat sparingly soluble in methyl alcohol (Found : *M*, 351·1; iod. val., 71·9. $C_{23}H_{44}O_2$ requires *M*, 352; iod. val., 72). The *ethyl* ester is a viscid oil, b. p. 243°/8 mm.

*Oxidation of Methyl* iso*Erucate with Potassium Permanganate.*—Methyl *iso*erucate (50 g.) was dissolved in acetone (500 c.c.), and potassium permanganate (168 g.) gradually added. The oxidation proceeded vigorously and sufficient heat was generated to keep the acetone boiling. The reaction mixture was heated on the water-bath for 15 hours, the acetone distilled off, and the manganese dioxide sludge dissolved by the addition of dilute sulphuric acid and sodium bisulphite. The oil which had separated was dissolved in ether, and the ethereal extract was washed with sodium carbonate solution until no further acid was removed, dried, and evaporated (A). The sodium carbonate extract was mixed with an excess of sodium hydroxide solution, boiled for one hour, and acidified. The liberated organic acids were dissolved in ether; on removal of the solvent a semi-solid, crystalline mass remained (47 g.). The mixture of acids was digested with light petroleum (b. p. 40—60°), and the boiling solution filtered (residue B), a small quantity of solid which separated on cooling being added to B. The light-petroleum extract was evaporated and the liquid acids (20 g.) were distilled; a large fraction was then obtained, b. p. 230—270°/685 mm. The residue in the distilling flask (4 g.) crystallised and was added to B. On refractionation, a fraction was obtained, b. p. 232—235°/685 mm., which was identified as *n*-octoic acid by titration (Found : *M*, 146. Calc. : *M*, 144) and by preparation of the *p*-toluidide, m. p. 67—69°. This m. p. was not depressed on admixture with an authentic specimen (Found : N, 6·1. Calc. : N, 6·0%). It was not found possible to separate a constant-boiling fraction from the residue.

The solid acid (B), m. p. 80—100°, was a mixture which could not be resolved by fractional crystallisation. Preliminary experiments having shown that one of the acids yielded a magnesium salt which was readily soluble in water, the mixture of acids was dissolved in dilute sodium hydroxide solution (phenolphthalein), and the boiling solution treated with an excess of magnesium sulphate. The sparingly soluble magnesium salt, $B_1$, was collected after 12 hours, and the filtrate acidified; a voluminous, white precipitate then separated. This was taken up with ether (yield, 9 g.) and recrystallised from hot water and finally from ethyl acetate, flat needles being obtained (Found: C, 63·0; H, 9·6; *M*, 230·6. Calc.: C, 62·6; H, 9·5%; *M*, 230). It melted at 126—127°, alone or mixed with decane-ακ-dicarboxylic acid, prepared by Walker and Lumsden's method (*loc. cit.*).

The sparingly soluble magnesium salt $B_1$ was decomposed with dilute sulphuric acid. The acid thus obtained (16 g.), m. p. 90—95°, softening at 80° (*M*, 255·6), was fractionally converted into the magnesium salt, four fractions being obtained. Titration showed that the last fraction, which was soluble in water, was mainly decane-ακ-dicarboxylic acid (*M*, 235); this was also present in not inappreciable amount in fraction 3 (*M*, 247·4). The first two fractions (*M*, 259; 256), which were evidently identical, were combined and recrystallised from ethyl acetate; an acid then separated in leaflets, m. p. 121—122° (Found: C, 65·1; H, 10·3; *M*, 258·9. Calc.: C, 65·1; H, 10·1%; *M*, 258). The barium salt also was analysed (Found: Ba, 34·8. Calc.: Ba, 34·9%). This acid has the properties of dodecane-αμ-dicarboxylic acid (Brown and Walker, *Annalen*, 1891, **261**, 123); direct comparison was not possible, but the methyl ester prepared from the silver salt separated in needles, m. p. 41°, which is stated to be the m. p. of methyl dodecane-αμ-dicarboxylate.

The neutral oil A (see above; 9 g.) consisted of unchanged methyl *iso*erucate.

The actual yields of the oxidation acids obtained and those calculated on the assumption that *iso*erucic acid is an equimolecular mixture of the two unsaturated acids, allowance being made for the weight of methyl *iso*erucate recovered, are: monobasic acids obtained, 16 g.; calc., 17·8 g.; dibasic acids obtained, 26 g.; calc., 28·2 g.

*Oxidation of Ethyl* iso*Erucate with Ozone.*—In a preliminary experiment made with the object of determining the most suitable conditions for the oxidation of ethyl *iso*erucate, erucic acid (10 g.) was oxidised with ozone, followed by chromic acid, under the conditions described below. The mixture of acids was taken up with ether

and on removal of the solvent an oil was obtained which partly crystallised. The solid, which melted at 109° after being washed with light petroleum and at 112—113° after crystallisation from benzene, was identified as brassylic acid by the method of mixed m. p. and by titration (Found: *M*, 243. Calc.: *M*, 244). The original filtrate, on dilution with light petroleum, deposited a further quantity of brassylic acid (m. p. 110°), and after the removal of this it was fractionated, b. p. 249—252°/685 mm., leaving a small residue which crystallised and probably consisted of brassylic acid, but was not further examined. The distillate was identified as pelargonic acid by titration (Found: *M*, 159·5. Calc.: *M*, 158).

Ozone was passed through a well-cooled solution of ethyl *iso*erucate (10 g.) in acetic acid (70 c.c.) until a test portion no longer decolorised bromine. After the addition of formic acid (10 c.c.), the solution was heated on the water-bath for 2 hours, cooled, and treated with an aqueous solution of chromic acid sufficient in quantity to convert the aldehydes present into the corresponding carboxylic acids. The mixture of acids (from 30 g. of ethyl *iso*erucate) was dissolved in ether and, after removal of the solvent, converted into the ethyl esters. On distillation under diminished pressure (8 mm.), the following fractions were obtained: (i) up to 150° (14 g.), (ii) 150—180° (5 g.), (iii) 180—190° (8 g.), (iv) 190—210° (6 g.), (v) above 210° (3 g.). Fraction (i) consisted of the esters of the monobasic acids and was not further examined; fraction (v) crystallised on keeping and was identified as ethyl arachidate, m. p. 50° (m. p. of acid, 77°) (Found: *M*, 311. Calc.: *M*, 312).

Since on redistillation the intermediate fractions could not be obtained pure, they were combined and after hydrolysis the acids were separated by the magnesium salt method described above. The fractions of the soluble and the insoluble magnesium salts were converted into the methyl esters through the silver salts; the soluble magnesium salt then yielded a methyl ester, b. p. 175—177°/10 mm. This was *methyl decane-*$\alpha\kappa$*-dicarboxylate*, since on hydrolysis it gave decane-$\alpha\kappa$-dicarboxylic acid, m. p. 126—127° (Found: *M*, 230·6. Calc.: *M*, 230).

The methyl ester from the acid yielding the sparingly soluble magnesium salt distilled at 191—192°/10 mm. and solidified on keeping; it melted at 41° after crystallisation from methyl alcohol. The acid obtained on hydrolysis had m. p. 121° (Found: *M*, 257·6. Calc.: *M*, 258).

*Oxidation of Erucic and Brassidic Acids.*—Erucic acid, on oxidation in alkaline solution under the conditions used by Lapworth and Mottram (J., 1925, **127**, 1629) for oleic acid, gave the high-melting dihydroxybehenic acid (m. p. 127—128°; yield 36%). In cold

acetone solution, it gave the low-melting isomeride, m. p. 99—100°. Under similar conditions, brassidic acid yielded only the low-melting dihydroxy-acid.

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## LVIII.—*Overpotential at Antimony Cathodes and Electrolytic Stibine Formation.*

By HENRY J. S. SAND, JULIUS GRANT, and WILLIAM VERNON LLOYD.

As is well known, two methods yielding different results are in common use for the measurement of electrolytic polarisation, *viz.*, the "direct" and the "commutator" method. In the former, the *P.D.* between the working electrode and the liquid in immediate contact with it is measured *during* the passage of the current and compared with that found in the absence of current; in the latter, the same *P.D.* is measured as soon as possible *after* interrupting the current. The attitude taken up by one of us (H. J. S. S.) to results obtained by the former method has been that only that portion of the measured *P.D.* should be considered to be a polarisation which is definitely proved to be so by the latter method. To indicate this attitude, the term *transfer-resistance* introduced by Gore (*Proc. Roy. Soc.*, 1885, **38**, 209; also numerous papers in *Phil. Mag.*) was revived in 1909 by Sand and Black (*Z. physikal. Chem.*, 1910, **70**, 496). This term has since been extensively used by Newbery (*Trans. Faraday Soc.*, 1919, **15**, 126) and others. The term may appear to imply definitely the irreversible character of the phenomenon measured, and, in so far as its unknown character was primarily to be indicated, it is now recognised that the term *transfer-impedance* would better comprise both reversible and irreversible effects. Both the direct and the commutator method have been extensively criticised without finality having been reached; but it is remarkable that very little attention has been hitherto directed to the entirely different character of the results obtained by the two methods. Whilst the direct method appears to lead to the conclusion that polarisation increases indefinitely with *C.D.*, the commutator method always yields results which point definitely to the existence of a maximum of polarisation. Experiments are now recorded which were carried out to determine whether there is any indication in the current density–polarisation (overvoltage) curves, determined by the direct method, of the polarisation-maxima shown by the commutator method.

## Experimental.

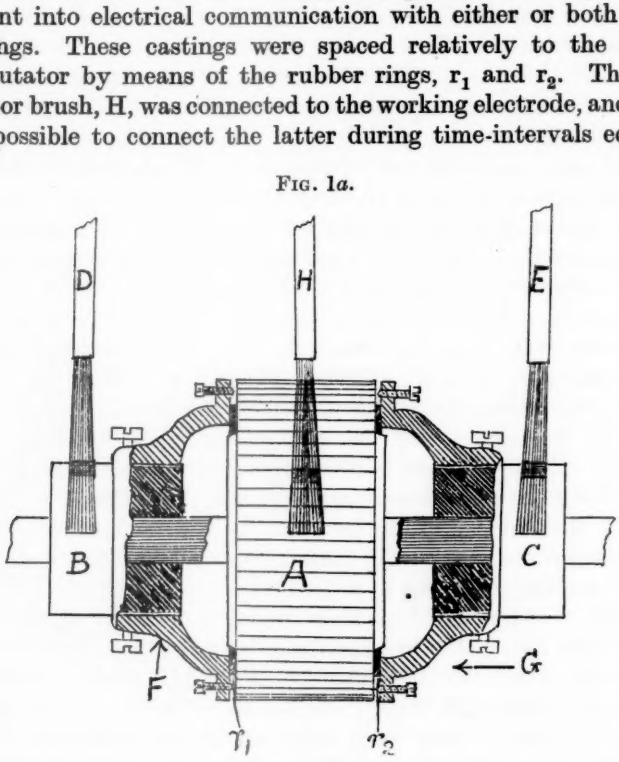
An antimony electrode was used as in previous work (Sand, Weeks, and Worrell, J., 1923, **123**, 456; Sand and Weeks, J., 1924, **125**, 160). An advantage of this metal is that it allows the phenomenon of polarisation to be studied in conjunction with that of hydride formation. The experiments reported by Sand, Weeks, and Worrell (*loc. cit.*) were repeated. We very much regret that we have been unable to confirm the numerous and detailed reports of his experiments supplied by Mr. Worrell, even when working with the same materials and apparatus. We are unable to account for these reports and wish to sever all association with them. The reports furnished by Mr. Weeks we have confirmed in general outline, but not in detail. The experimental arrangements used have been in part further developed for the purposes of the present investigation. The electrolytes employed were: (1) Solutions of various acids in varying concentrations; (2) solutions of acids containing salts; and (3) solutions of alkaline substances.

The main points studied have been (1) the dependence of polarisation on the time which has elapsed since the breaking of the current; (2) the relation between the overvoltage–current density curves for a given solution and electrode, determined on the one hand by the direct and on the other by the commutator method; (3) the relation between the values obtained and the composition of the solution, including hydrogen-ion concentration; and (4) the dependence of hydride formation on the conditions of the experiment. The first point has been studied for other electrodes by a number of workers (Glasstone, J., 1923, **123**, 2926; 1924, **125**, 250, 2646; 1925, **127**, 1824; *Trans. Faraday Soc.*, 1924, **19**, 808; Knobel, *J. Amer. Chem. Soc.*, 1924, **46**, 2613; Newbery, J., 1924, **125**, 511; *Proc. Roy. Soc.*, 1925, *A*, **107**, 486; 1926, *A*, **111**, 182). Whereas Glasstone and Knobel employed mechanical commutators, Newbery used the cathode-ray oscillograph. The method employed in the present investigation belongs to the class employed by the first-named authors, but the apparatus allows readings to be made after very much shorter time-intervals than have been hitherto attempted.

Figs. 1*a* and 1*b* illustrate the principle of the commutator employed. In the design and construction of this instrument we have had the assistance of Messrs. F. S. M. and J. F. Wright, of Messrs. F. Cox, Ltd., which we gratefully acknowledge. The apparatus consists essentially of a 64-segment dynamo commutator of commercial construction, A, which was mounted on the same spindle with two insulated slip-rings, B and C, the latter being in communication

through the wire brushes, D and E, with the source of current and the potentiometer, respectively. To each slip-ring was screwed a cup-shaped casting, F and G, each of which was supplied with 64 screw-holes and screws that were placed opposite the 64 segments of the commutator. It was thus possible to bring any one segment into electrical communication with either or both of the slip-rings. These castings were spaced relatively to the central commutator by means of the rubber rings, $r_1$ and $r_2$. The commutator brush, H, was connected to the working electrode, and it was thus possible to connect the latter during time-intervals equal to

FIG. 1*a*.

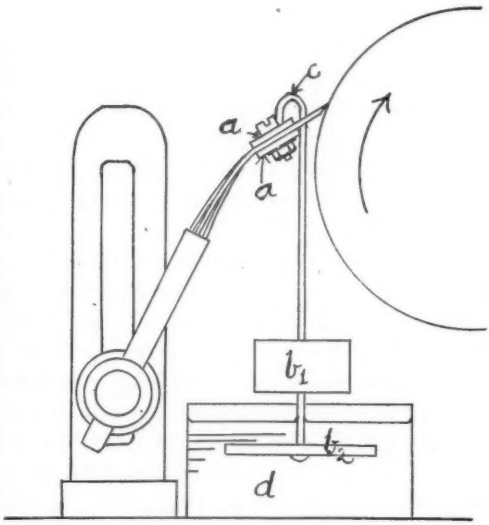



that of 1/64 of a revolution to either the source of current or the potentiometer. Thus, if 32 successive segments were connected to the current slip-ring B, 32 being left unconnected to B; if, further, these latter were connected individually in successive experiments to the potentiometer slip-ring C; and if the number of revolutions of the commutator was $r$ per min., the current would pass through the cathode during $32/64r$ min. and would be off for an equal time, during which the average cathode potential could be measured in intervals of $1/64r$ min. An ordinary bearing was at first employed but, later, ball-bearings were fitted. The spindle of the commutator was driven by means of a pulley and belt from an electric motor, and the drive was sufficiently powerful to allow a speed counter to be pushed against the spindle without slowing it

down appreciably. The speed at which the instrument was run in many of the experiments recorded was 4200 revs. per min.

The main difficulty encountered was due to electrical leakage. General electric leakage from outside was obviated by placing the apparatus on insulating material which lay on earthed metal plates. To prevent leakage across the segments, which was apt to occur owing to metal or other dust, it was necessary to brush out the apparatus. For this purpose, all parts of the commutator were accessible after the screws locking the castings F and G had been loosened and the latter had been pushed back. An ordinary brass wire brush, as indicated in Fig. 1*a*, was at first employed; later, however, it was replaced by a copper brush the construction of which is explained in Fig. 1*b*. This consisted of 13 copper wires, of about 16 wire-gauge, which were soldered into a brass holder and spread out into a flat band by clamping them between the two plates *a*, *a*. The wires were cut off obliquely in the manner shown, so as to form a contact along a straight line on the commutator surface. In order to prevent the brush from vibrating unduly, it was weighted by means of the weights $b_1$, $b_2$ amounting altogether to about 150 g. These were hung from *a*, *a* by means of the hook *c*, and their motion was damped by placing $b_2$ in oil contained in the dash pot *d*. The mica insulation between successive segments of the commutator was cut away at the top for a distance of about 1 mm. in order to obtain a sharper break. A difficulty met with when a large number of successive segments was connected simultaneously to the same slip-ring was due to the fact that tightening up one screw tended to loosen its neighbours. To obviate this, only one or two screws were employed to make the connexion to the slip-ring, and the successive segments were put into communication with each other by means of pieces of tin foil that were held down by a rubber band slipped over the commutator.

FIG. 1*b*.



The efficiency of the instrument is of the same order as that of the cathode-ray oscillograph. Thus, large numbers of experiments were carried out in which the average potential was measured during $2{\cdot}2 \times 10^{-4}$ sec. after the breaking of the current, which is approximately the instantaneous potential after $1{\cdot}1 \times 10^{-4}$ sec. The smallest times after the breaking of the current recorded by Glasstone are $20 \times 10^{-4}$ sec., and the corresponding shortest time shown by Knobel in his curves is $5 \times 10^{-4}$ sec.

Currents were measured in all experiments by moving-coil ammeters suitably shunted. Where intermittent current is employed, such instruments do not register the instantaneous value of the current, but act with sufficient accuracy as coulombmeters (J., 1923, **123**, 2896). It must therefore be understood that all current densities are stated in millicoulombs/sec./sq. cm., even where for brevity the term "milliamperes" is employed. Where measurements by the direct method were made in alternation with those by the commutator method, the former were carried out by introducing a short-circuit between the current slip-ring brush and the commutator brush without altering any other connexion.

The electrolytic apparatus was approximately the same as that hitherto used, but was adapted to the measurement of the cathode potential by the direct method. As in previous work, the electrolyte in the hydrogen-electrode chamber was the same as that around the cathode. Hydrogen was kept bubbling continuously through it, and, except in some of the experiments on yields of stibine, was afterwards led past the exposed surface of the cathode. The method of measuring the yield of stibine was generally the same as that previously employed, *i.e.*, the hydrogen issuing from the cathode chamber was passed through a solution of silver nitrate and the increase of weight determined. The method might perhaps be criticised on the ground that hydrogen, even when purified carefully, is found always to precipitate small amounts of silver from silver nitrate solutions, the increase of weight thus produced being equal to that of the hydrogen absorbed. This increase was, however, negligible in all cases. Thus, in an experiment in which 1000 c.c. of dried hydrogen were bubbled slowly through the silver nitrate absorption bulbs, the total increase in these *plus* the calcium chloride tubes was found to be less than 2 mg., corresponding to a calculated volume error in the ratio of stibine to hydrogen of only about 3 parts in 10,000 parts. In many of the experiments, yields of stibine were determined by passing the issuing gas through a heated quartz tube of about 3 mm. bore and estimating the increase of weight. In no case

was a perceptible difference obtained between such experiments and those in which silver nitrate solution was employed.

*Results in Acid Solution.* (*Experiments by* W. V. LLOYD.)

*Solutions of Acids in the Absence of Salts.*—Experiments were first carried out on the reproducibility of results. Most of these were performed with one of the commutators used in former work. Hydrogen was bubbled past the electrode, as previously explained. With a definite commutator speed at a given temperature, closely reproducible results were obtained. In a series of experiments it requires about 10 minutes to polarise the antimony cathode to its maximum, a *C.D.* slightly over the critical value being used. After this, results are reproducible, under carefully controlled conditions, to within a few millivolts. The material of the electrodes was purchased at various times and was the purest obtainable. Some of the antimony bars were obtained as such; others were cast from powder. A series of experiments showed that, when the antimony was suspended from platinum wires, or when platinum was wound round it, the same values of overvoltage were ultimately obtained, but these took longer to establish themselves. The antimony appeared to be very little attacked in these experiments and the surface was only very slightly dulled. The electrodes were polished by means of fine emery paper before the experiments.

A large number of readings were taken with the commutator shown in Fig. 1*a*, to determine the relation between polarisation and time for various intervals after interrupting the current, and with various *C.D.*'s. A complete study of polarisation was made in the case of *N*-, 4*N*-, and 16*N*-sulphuric acid. Thirty-two segments of the commutator were connected to the current slip-ring, and the potentiometer slip-ring was successively connected to each of the other thirty-two. The speed of the commutator was 4200 revs. per min.; the readings on the potentiometer thus represent average polarisations during $2{\cdot}2 \times 10^{-4}$ sec. and the current was alternately on and off during 1/140 sec. The results of the study of *N*-sulphuric acid have been graphically represented in Fig. 2 in such a manner as to give (1) for each segment a curve representing the relation between overvoltage and *C.D.*, and (2) for each *C.D.* a curve indicating the relation between overvoltage and time since the breaking of the current. To make this possible, all voltages are plotted as ordinates on the same scale and have the same zero. Current densities are plotted as abscissæ, likewise all on the same scale, but they start from different zeros for each segment. These zeros have been made recognisable for each current density–overvoltage curve by arbitrarily extrapolating it

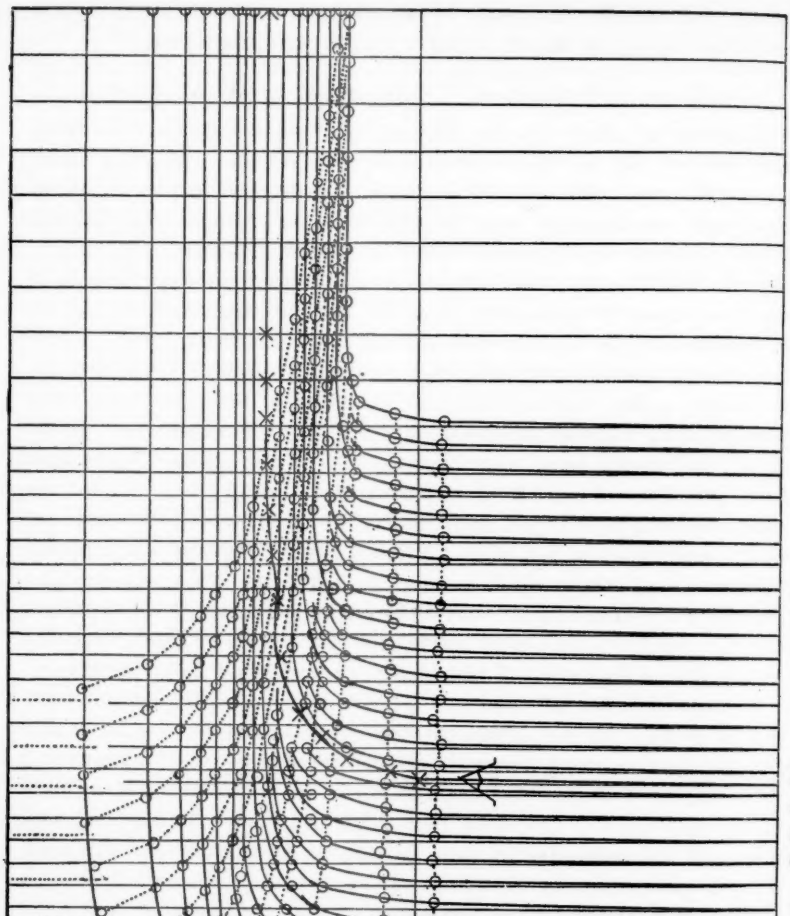



FIG. 2.

backwards to zero overvoltage for zero *C.D.* The current density zeros for successive segments have been placed at an equal distance from each other, and since the time interval between the polarisations on such segments was $2{\cdot}2 \times 10^{-4}$ sec., this time interval is

also represented by the distance chosen. Points corresponding to overvoltages measured on successive segments for the same *C.D.*'s have therefore been connected by dotted curves which may be termed decay curves, and represent the rate of decay of overvoltage with time. The zero line of the abscissæ of each dotted curve has also been dotted in as a vertical line. The current density–overvoltage curve, corresponding to the combined effect of 30 segments simultaneously connected to the potentiometer, has been drawn for purposes of comparison half-way between the curves belonging to the two middle segments and is indicated by A. The following new facts emerge. (1) For each individual segment the polarisation rises to a maximum which it maintains constant in every case for *C.D.*'s between about 8 and 100 milliamps./sq. cm. In the case of the segments furthest removed from the break of the current, the maximum is attained at a *C.D.* below 2 milliamps./sq. cm. At *C.D.*'s above 100 milliamps./sq. cm. there is a slight decrease in polarisation, which may probably be explained by local heating. (2) The sharpest drop in polarisation occurs between the first and second segments. It is therefore unsatisfactory to extrapolate to zero time from values obtained on later segments, as advocated by Glasstone (*loc. cit.*). The first reading employed by this investigator in his studies of overvoltage of other metals corresponds approximately to the fourth point of the dotted decay curves shown in our diagram. It will be apparent from the first three additional points given here, that in the absence of an agreed equation, extrapolation leads to quite uncertain results. We therefore suggest that polarisation is best expressed by stating not only its value but also the time-interval during which it is measured. In many cases it might be sufficient to state the mean time between the beginning and end of the measurement. (3) The curves show that, when overvoltage on antimony electrodes in $N$/1-sulphuric acid does not exceed about 0·45 volt, it maintains itself sensibly constant over the whole range examined of 1/140 sec.

For the further study of polarisation, overvoltages obtained by the direct and by the commutator methods in the same solutions were compared. A thorough study was made of solutions of sulphuric acid in strengths varying from $16N$ to $N/160$; of hydrochloric acid ($4N$ to $N/16$); of phosphoric acid ($8N$ to $N/16$); and of $N$/1-oxalic acid. Some of the numbers obtained for $N$/1-sulphuric acid are recorded in Table I, those for the other electrolytes being similar in general character. The commutator overvoltages were obtained by means of the Whetham commutator employed in previous investigations and are average polarisations during the first 0·0059 sec. after breaking the current. Measurements by the

TABLE I.

| | ($N$-$H_2SO_4$.) | | | | |
|---|---|---|---|---|---|
| Milliamps./cm.$^2$ ..... | 0·06 | 0·18 | 0·31 | 0·50 | 0·63 |
| Millivolts (Comm.)... | 322 | 383 | 415 | 447 | 467 |
| ,, (Dir.) ..... | 331 | 398 | 428 | 459 | 477 |
| Milliamps./cm.$^2$ ..... | 0·75 | 0·87 | 0·98 | 3·0 | 4·9 |
| Millivolts (Comm.)... | 483 | 496 | 509 | 557 | 559 |
| ,, (Dir.) ..... | 492 | 507 | 520 | 618 | 658 |
| Milliamps./cm.$^2$ ..... | 6·9 | 8·8 | 11·7 | 17·7 | 21·6 |
| Millivolts (Comm.)... | 559 | 559 | 559 | 559 | 559 |
| ,, (Dir.) ..... | 685 | 704 | 725 | 755 | 770 |
| Milliamps./cm.$^2$ ..... | 25·5 | 29·5 | 43·7 | 70·0 | 87·5 |
| Millivolts (Comm.)... | 558 | 558 | 556 | 554 | 554 |
| ,, (Dir.) ..... | 784 | 796 | 840 | 903 | 935 |
| Milliamps./cm.$^2$ ..... | 105 | 122 | 140 | 166 | 184 |
| Millivolts (Comm.)... | 552 | 552 | 552 | 550 | 548 |
| ,, (Dir.) ..... | 964 | 988 | 1014 | 1049 | 1075 |
| Milliamps./cm.$^2$ ..... | 201 | 219 | 236 | 262 | |
| Millivolts (Comm.)... | 548 | 546 | 546 | 546 | |
| ,, (Dir.) ..... | 1092 | 1106 | 1119 | 1138 | |

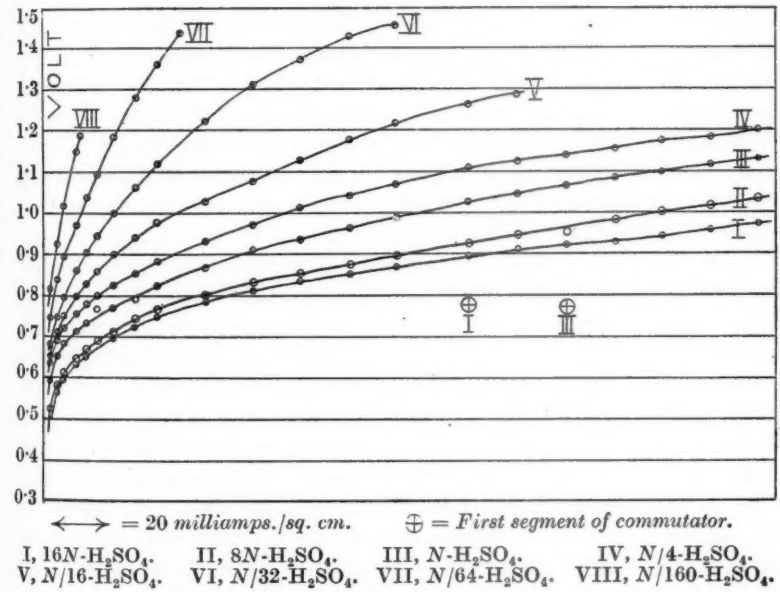
direct method were made alternately with those by the commutator method for each *C.D.* It will be seen that for low polarisations up to and slightly beyond 0·45 volt, the value previously mentioned, overvoltages measured by the direct and by the commutator method are sensibly identical, when expressed in coulombs/sec./sq. cm.

The further study of the results is best made in conjunction with Fig. 3 in which current density–overvoltage curves, obtained by the direct method, are plotted for solutions of sulphuric acid of various strengths. It will be seen that at high *C.D.*'s increases in direct overvoltages become nearly proportional to increases in *C.D.* For very high *C.D.*'s, however, such as those for which the commutator overvoltages begin to show a decrease, there is a falling off from the linear relation. The simplest way to explain this phenomenon is to assume that at high *C.D.*'s an almost constant transfer- (or surface) resistance establishes itself, which, however, shows a tendency to decrease with increase of the *C.D.* to extremely high values. The overvoltage measured should then be equal to the sum of a true polarisation $\omega$, plus a term $i\kappa$, where $\omega$ is a value approaching the commutator overvoltage extrapolated to zero time-interval, $i$ is the current density, and $\kappa$ is the transfer-resistance per unit surface. Commutator overvoltages, determined by measurement on the first segment of the interval commutator, are shown separately on the diagram for 16$N$- and $N$-acid. It can be seen that in the case of the strong solutions of sulphuric acid the commutator overvoltage thus determined is almost identical with the voltage indicated by the ordinate corresponding to zero current density on the asymptote found by the direct method. In

the case of the other solutions shown, there is an approximation to a like result. Phosphoric acid solutions gave results similar to those found with sulphuric acid. In hydrochloric and oxalic acid solutions, the differences between the commutator- and the extrapolated direct-method overvoltages were considerably greater than with sulphuric and phosphoric acids.

*Relation between Overvoltages and the Composition of the Solution.*—To investigate this, overvoltages were determined for a large number of electrolytes by means of the Whetham commutator giving average polarisations corresponding to an interval of 0·0059

FIG. 3.




⟷ = 20 *milliamps./sq. cm.* ⊕ = *First segment of commutator.*

I, 16*N*-$H_2SO_4$. II, 8*N*-$H_2SO_4$. III, *N*-$H_2SO_4$. IV, *N*/4-$H_2SO_4$.
V, *N*/16-$H_2SO_4$. VI, *N*/32-$H_2SO_4$. VII, *N*/64-$H_2SO_4$. VIII, *N*/160-$H_2SO_4$.

sec. after breaking the current. The maximum values (critical overvoltages) for some of the sulphuric acid solutions examined are assembled in Table II.

TABLE II.

(Sulphuric acid solutions.)

| Conc. ..... | 16*N*. | 8*N*. | 4*N*. | 2*N*. | *N*. | *N*/4. | *N*/16. | *N*/32. | *N*/64. |
|---|---|---|---|---|---|---|---|---|---|
| Volts ..... | 0·522 | 0·524 | 0·537 | 0·547 | 0·559 | 0·557 | 0·560 | 0·576 | 0·587 |

It will be seen that the variation of overvoltage with concentration of the sulphuric acid is only slight, but there is a distinct rise with decrease of concentration throughout. Part of this may possibly be due to concentration polarisation set up by local dilution of

the electrolyte, particularly in the case of the very dilute electrolytes. The values given were obtained with stirring by means of a rapid current of hydrogen. The overvoltages obtained in other acid electrolytes are very close to those quoted. Thus, overvoltages in phosphoric acid are almost identical with those found for sulphuric acid of the same $p_H$, whereas overvoltages in hydrochloric and oxalic acids are about 2 centivolts higher. The overvoltage found for tartaric acid was distinctly abnormal. It first assumed a value about 5 centivolts below that of other acids, and after the cathode had been in the electrolyte for about 45 minutes a further decrease of 7 centivolts was observed. It was also noted that during electrolysis for a few minutes the cathode assumed a dark colour. Further, when the cathode was left standing in fresh tartaric acid solution over-night, a small amount of antimony went into solution. The abnormal behaviour of tartaric acid with regard to overvoltage should be considered in conjunction with the abnormally high yield of stibine obtained in this electrolyte (*vide infra*). The results obtained are in general agreement with those found by Glasstone for lead and mercury cathodes (J., 1924, **125**, 2414, 2416).

*Acid Solutions containing Alkali Salts.*—Solutions of the following acids containing also their sodium salts were studied: Sulphuric, hydrochloric, phosphoric, and acetic. The original object of the experiments was to trace a connexion between the $p_H$ value of the solution and the maximum (characteristic) overvoltage observed. For this purpose solutions of the pure acid were usually employed initially, and to these, successive quantities of sodium hydroxide solution were added. No simple results were obtained, however. The principal conclusions drawn were the following. (1) When the concentration of the alkali salt and the *C.D.* are not very high, overvoltage values are obtained which are either identical with, or only slightly higher than, those of pure acids having the same $p_H$ value, and the appearance of the cathode is similar to what it would have been in the solution of the pure acid. Thus a *N*-solution of sulphuric acid gave a $p_H$ voltage of 0·273 and an overvoltage of 0·538, whereas a similar solution which was also *N*/2 with respect to sodium sulphate gave a $p_H$ voltage of 0·269, and an overvoltage of 0·559. On the other hand, when the quantity of acid was small relatively to that of the alkali, wholly different results were obtained. A very much higher *C.D.* and a longer time were required to establish the maximum overvoltage and the results were not so definite. The electrode appeared to be covered with a black deposit after an experiment, such as is met with when alkaline electrolytes are used. The final results were entirely different from those obtained

with pure acid solutions of the same $p_H$. Thus a solution which was $N$ with regard to sodium sulphate and approximately $N/25$ with regard to sulphuric acid required a *C.D.* of about 80 milliamps./sq. cm. to establish the maximum overvoltage of 1·245 volt. A solution containing only acid and having the same $p_H$ voltage of 0·374 would have shown an overvoltage smaller by about 0·67 volt. Similarly, a solution which was approximately $N$ with regard to phosphate and to which enough sodium hydroxide was added to give it a $p_H$ voltage of 0·355 had not attained a constant overvoltage even for a *C.D.* of 140 milliamps./sq. cm. The overvoltage then was 0·85 volt as compared with 0·57 volt for a sulphuric acid solution of similar $p_H$ value. Results of this kind were obtained whether the porous diaphragm or the bottle apparatus was used. They point to considerable concentration changes in the boundary layer at the electrode.

*Yields of Stibine.*—A lengthy series of experiments on yields of stibine in acid solution showed that stibine is formed only with great difficulty and in small yield. A scarcely perceptible unsteadiness in overvoltage is the only indication of the evolution of the gas. Experiments were carried out in which antimony cathodes were employed in solutions of sulphuric, hydrochloric, and tartaric acids. Further, both antimony and lead cathodes were used in solutions of the same acids to which antimonious or antimonic compounds had been added. Direct, intermittent, and alternating currents were used. The last named consisted of alternating pulses of direct current obtained by means of a rotating commutator from a continuous current supply, the strength of the pulses in either direction being capable of independent adjustment and measurement (J., 1926, 2971). The following is a brief survey of the results obtained, none of which confirmed those reported by Worrell (*loc. cit.*). No stibine was formed in $N$-sulphuric or hydrochloric acid with continuous current with *C.D.*'s up to about 100 milliamps./sq. cm. At a *C.D.* of 112 milliamps./sq. cm. an unweighable trace of the gas was detected. Smooth electrodes and electrodes roughened by previous electrolysis, both in acid alone and in acid containing antimony sulphate, were tried. The highest yield obtained in sulphuric acid solution was 0·25% with 16$N$-acid and continuous current of 1600 milliamps./sq. cm. density. In hydrochloric acid, similar figures were obtained. When alternating current was employed in 4$N$-hydrochloric acid, a *C.D.* of 30 millicoulombs/sec./sq. cm. when the working electrode was the cathode, and of 12 when it was the anode, sufficed to produce a yield of 0·3%. The yields obtained by continuous-current electrolysis of tartar emetic in tartaric acid solution were higher than

those in other electrolytes. The electrode here becomes covered with a voluminous, black, spongy deposit. The highest yield obtained hitherto is 2·34%. This was found when a solution of *N*-tartaric acid was electrolysed with an alternating current of 7·8 milliamps./sq. cm. while the working electrode was the cathode, and of 2·9 while it was the anode. In general, it may be said that high *C.D.*'s are necessary for stibine formation. A limit is, however, soon reached in practice owing to heating of the electrolyte. Special experiments showed that when a hot electrolyte was used initially, no stibine was obtained in any circumstances. With both sulphuric and hydrochloric acids, a high concentration favours the formation of stibine, and results were given by very much lower *C.D.*'s with alternating than with direct current.

*Results obtained in Alkaline Solution.* (*Experiments by* J. GRANT.)

In the experiments in alkaline solution, hydrogen was always bubbled through the liquid. It was found particularly necessary to do this when the direct method was employed in order to remove small bubbles from the mouth of the glass capillary leading to the hydrogen electrode. Considerably more time elapsed in these experiments before readings became constant than in those in acid solution. It varied in different cases from 5 to about 30 minutes, but the final results were repeatable. Overvoltages in the following solutions were studied: 8*N*-, *N*-, and *N*/10-Sodium hydroxide; *N*-sodium carbonate and -sodium hydrogen carbonate; half-saturated baryta, calcium hydroxide, and disodium hydrogen phosphate; *N*-ammonium hydroxide and -ammonium carbonate; approximately *N*/45- and *N*/19-tetramethylammonium hydroxide; *N*/37-tetraethylammonium hydroxide; and *N*-sodium sulphate. The temperature was in all cases about 20°.

Table III gives overvoltages determined both by the direct and by the commutator method in solutions of *N*-sodium hydroxide and half-saturated baryta. These results may be taken as representative of those obtained in other solutions. Current densities are recorded in the first line in milliamps./sq. cm. under the heading *C.D.* (see p. 382). The overvoltages are assembled in the other lines, and are stated in millivolts. They are classified according to the solution and type of measurement—direct or commutator—as NaOH, *d*; NaOH, *c*; etc. The commutator employed for the latter gave average polarisations during the first 0·0137 sec. after breaking the current in the case of baryta, and in the case of the sodium hydroxide both 0·008 and 0·005 sec. were used without alteration of the results. It will be seen that, as in acid solution, the results obtained in a given electrolyte by the direct and com-

mutator methods do not differ much for a given *C.D.* as long as this is small. The large divergences only occur at higher *C.D.*'s.

TABLE III.

| *C.D.* ..... | 0·2 | 0·3 | 0·5 | 0·7 | 1·5 | 5·0 | 10·0 | 12·5 | 15 | 20 | 40 | 170 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NaOH, *c* | 390 | 420 | 455 | 525 | 550 | 635 | 690 | 710 | 715 | 715 | 715 | 715 |
| NaOH, *d* | 200 | 355 | 500 | 530 | 585 | 655 | 800 | 840 | 920 | 1600 | — | — |
| $Ba(OH)_2$, *c* | 115 | 190 | 325 | 350 | 495 | 595 | 635 | 635 | 635 | 635 | 635 | 635 |
| $Ba(OH)_2$, *d* | 135 | 255 | 455 | 535 | 590 | 640 | 995 | 1160 | 1250 | 1800 | — | — |

The decay of polarisation was also determined by means of the new commutator, the interval during which a measurement was made being 1/4000 sec. In Table IV, the mean times, *t*, of these intervals and the polarisations ω are given for *N*-sodium hydroxide and half-saturated baryta for *C.D.*'s well above the critical values. The results for other solutions are similar in nature.

FIG. 4.

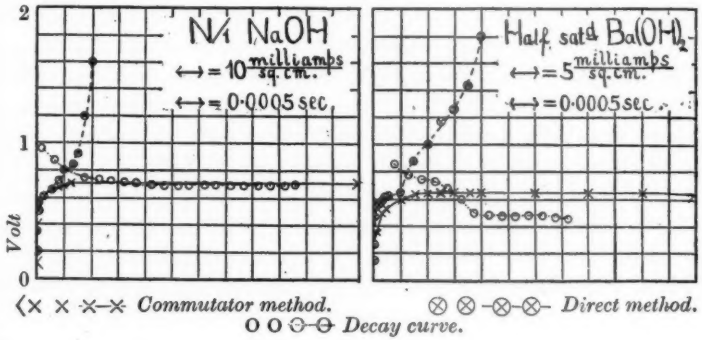



TABLE IV.

| *t* ($10^{-4}$ sec.). | | 1·25 | 3·75 | 6·25 | 8·75 | 11·25 | 13·75 | 16·25 | 18·75 |
|---|---|---|---|---|---|---|---|---|---|
| ω | NaOH | 945 | 870 | 795 | 750 | 745 | 730 | 720 | 715 |
| (Millivolts) | $Ba(OH)_2$ | — | 845 | 780 | 755 | 740 | 675 | 600 | 500 |
| *t* ($10^{-4}$ sec.). | | 21·25 | 23·75 | 26·25 | 28·75 | 31·25 | 33·75 | 36·25 | 38·75 |
| ω | NaOH | 700 | 695 | 690 | 690 | 690 | 690 | 690 | 695 |
| (Millivolts) | $Ba(OH)_2$ | 480 | 470 | 475 | 480 | 475 | 470 | 450 | — |

The numbers recorded in Tables III and IV are plotted in Fig. 4. The full lines refer to results obtained by the commutator method, the broken lines to those found by the direct method; the abscissæ are current densities and the ordinates overvoltages. It will be seen (1) that, as is known, the commutator overvoltage in every case reaches a constant maximum; and (2) that at voltages not far removed from these maxima, the overvoltage–current density curve determined by the direct method shows a distinct inflexion or bend, which appears to indicate the setting in of some constant-voltage

process absorbing considerable current and possibly of a chemical nature. The results of Table IV have been plotted into the diagram as dotted lines, and may be termed decay curves of polarisation; the abscissæ of these are times on the scale shown. It will be seen that the curves descend from a high polarisation value to one that remains nearly constant for a comparatively long time, and is not far removed from that indicated by the full curves. This again points to a large reserve of polarisation at certain voltages and indicates a chemical rather than a physical explanation. It may be connected with the formation of sodium alloys on the surface of the cathode.

Table V gives a summary of overpotentials found in alkaline solution. The overvoltages given under the heading $\omega_c$ in the second line were determined by means of one of the commutators; they are in most cases polarisations during the first 1/200 sec. after interrupting the current, some of them being averages of a number of determinations. On the line marked $\omega_d$ are assembled values of overvoltage which have been determined from the current density–overvoltage curves given by the direct method. These values are taken from the curves at positions as close as possible to where the inflexion occurs. The electrolytes are given in the order of decreasing $p_H$. It will be seen that, although there is a general increase of overvoltage with decreasing $p_H$, a number of the electrolytes examined fall out of line. There is thus no question of an accurate agreement with the relation previously proposed (J., 1924, **125**, 162), *viz.*, $\omega + 2h = c$, where $\omega$ is the overvoltage, $h$ the *P.D.* between a standard electrode and the hydrogen electrode in the solution examined, and $c$ a constant. The possibility cannot, however, be dismissed that we are dealing with a relation of the form proposed which is vitiated by secondary interfering influences. The matter is being further investigated also with electrodes other than antimony. Except in the case of sodium hydroxide solutions, there is no indication of any direct relation between sodium-ion concentration and overvoltage as was suggested by Herasymenko (*Rec. trav. chim.*, 1925, **44**, 503).

TABLE V.

| Solution. | 8*N*-NaOH. | *N*-NaOH. | $Ba(OH)_2$ (half-sat.). | *N*/10-NaOH. | *N*-$NH_4OH$. | $Ca(OH)_2$ (half-sat.). |
|---|---|---|---|---|---|---|
| $\omega_c$ (volt) ..... | 0·64 | 0·72 | 0·60 | 0·73 | 0·50 | 0·46 |
| $\omega_d$ (volt) ..... | | 0·70 | 0·65 | | | 0·90 |

| Solution. | *N*-$Na_2CO_3$. | *N*/37-$NEt_4OH$. | *N*/90-$NMe_4OH$. | $Na_2HPO_4$ (half-sat.). | *N*-$NaHCO_3$. | *N*-$Na_2SO_4$. |
|---|---|---|---|---|---|---|
| $\omega_c$ (volt) ..... | 0·74 | 0·87 | 0·93 | 1·22 | 0·94 | 1·24 |
| $\omega_d$ (volt) ..... | | 0·95 | | 1·20 | | 1·27 |

*Experiments on the Evolution of Stibine by Electrolysis in Sodium Hydroxide Solution.*—Reference has already been made to the fact that in alkaline solution the antimony cathode becomes blackened during electrolysis. Some antimony is always found dissolved in the solution after the experiments. The black deposit is loose and may be rubbed off with a finger. It appears to have little effect on overvoltage results. It is different in character from deposits obtained under similar conditions on metals such as cadmium which form insoluble hydroxides in alkaline solution. As the *C.D.* is increased a precipitate begins to deposit in the electrolyte. The supposition previously made, that it is formed from stibine which is primarily evolved, has been proved correct as will be shown below. The precipitate appears to have all the properties of metallic antimony. Experiments were also carried out in which hydrogen containing stibine was generated from hydrochloric acid containing tartar emetic by means of zinc and then passed through 8*N*-sodium hydroxide. A precipitate forms very slowly and again appears to have all the properties of finely-divided metallic antimony. We can in no wise confirm the statement made by Weeks and Druce (*Rec. trav. chim.*, 1925, **44**, 971) that either of these precipitates has the properties ascribed by these authors to their hydride (J., 1925, **127**, 1069). The total quantity of antimony present in solution and as metal appears to increase continuously with *C.D.* for a given amount of current. Experiments were carried out, in the manner recorded previously, in which the hydrogen generated electrolytically on the antimony cathode was collected after drying and passing through absorption apparatus for stibine. Only at very high *C.D.*'s was blackening in the latter noted. In 8*N*-sodium hydroxide, the maximum yield of stibine gas amounted to 0·18% by volume for a *C.D.* of 150 milliamps./sq. cm. (intermittent). Experiments were also performed in which the amounts of antimony precipitated as metal by intermittent current of various densities, and also the amounts which had dissolved, were determined, the electrolyte being *N*- or 8*N*-sodium hydroxide. From these experiments, yields of stibine were calculated on the assumption that all the antimony found owed its presence to the primary production of this gas. The yields thus found varied between 0·32 and 1·71% by volume for *C.D.*'s varying between 15 and 150 milliamps./sq. cm. The lowest *C.D.* at which the antimony precipitated as metal was weighable was 35 milliamps./sq. cm. for *N*-, and 50 for 8*N*-sodium hydroxide. After metallic antimony has begun to form, the amount going into solution does not increase appreciably with increasing *C.D.* The experience gained from these experiments suggested the possibility that if

hydrogen were blown rapidly past the working electrode it might carry the stibine with it before the latter had time to decompose. To test this, a small cone-shaped electrode was used, which pointed downwards towards the flared exit of a tube from which purified hydrogen was rapidly blown. The amount of hydrogen generated electrolytically was calculated from the current strength and time. The exposed area of the cathode varied in different experiments from 2 to 3·5 sq. cm. The results fully justified expectations, and prove that the antimony found distributed in the electrolyte has been formed from stibine primarily produced. The yields obtained in this way in *N*-sodium hydroxide are recorded in Table VI. It will be seen that the highest yield of stibine obtained as such amounted to 2%. It is noteworthy that with the very high *C.D.*'s the antimony cathode showed progressively less of the black deposit. The heating which occurs with high *C.D.* sets a limit to the yields. The experiments are being continued.

TABLE VI.

| Type of current. | Millicoulombs per sq. cm. | Yield %. As $SbH_3$. | Yield %. Sb in pot. | Yield %. Total. |
|---|---|---|---|---|
| Continuous | 150 | 0·22 | 0·05 | 0·27 |
| | 250 | 0·21 | 0·26 | 0·47 |
| | 500 | 0·13 | 0·24 | 0·37 |
| | 1000 | 0·47 | 0·56 | 1·03 |
| | 2500 | 2·03 | 0·42 | 2·45 |
| Intermittent | 20 | 0·12 | — | 0·12 |
| | 50 | 0·32 | 0·22 | 0·54 |
| | 200 | 1·10 | 0·56 | 1·66 |
| | 370 | 1·50 | 2·00 | 3·50 |

*Summary of Results and Conclusions.*

1. In all cases examined, the current density–overvoltage curves obtained by the direct method bear a relation to those found under corresponding conditions by the commutator method.

2. It has been shown that in acid solution small polarisations maintain their value practically constant for periods up to 1/140 sec. At higher *C.D.*'s the polarisations fall off rapidly with time, but in all cases the polarisation measured during a given time-interval after the breaking of the current assumes a maximum value independent of the polarising current. Even when the interval during which the measurement is made is only 1/5000 sec. after the breaking of the current, such a maximum is obtained, and there is thus a discontinuity between it and the polarisation value shown by the direct method, the latter increasing indefinitely with *C.D.* This is in agreement with results obtained by means of the cathode-ray oscillograph by Newbery (*loc. cit.*) for other cathodes, but not with

the views propounded by Knobel (*loc. cit.*) on what appears to the authors to be insufficient experimental evidence.

3. In the best-conducting solutions, the increase of overvoltage found by the direct method becomes almost proportional to increase of *C.D.* for high values of the latter. This may be taken as evidence that overpotential measured by the direct method at high *C.D.*'s consists of the sum of a true polarisation, which is almost independent of the *C.D.*, and a term which results from passing the current through a more or less constant resistance at the surface of the electrode.

4. Replacing Gore's term "transfer-resistance" by the term "transfer-impedance," to describe effects of which the irreversibility or otherwise has not been established experimentally, our results may be described by saying that, in some of the cases examined, transfer-impedance has been proved to be irreversible after 1/5000 sec.

5. The time–polarisation curve shows considerable change in direction on extrapolating it backwards to zero time, and we therefore recommend that the polarisation measured and the time-interval of its measurement should be stated, rather than that attempts should be made to extrapolate to zero time from a small number of measurements as advocated by Glasstone (*loc. cit.*). We have confirmed in a number of cases that the values obtained sufficiently closely represent the average polarisation during the time of measurement and that they are not greatly affected by slight variations of the latter.

6. Overpotentials found in acid solution increase slightly with dilution. The effect is, however, smaller than corresponds to the relation $\omega - h = c$, in which the symbols have the significance attached to them above (p. 392). Experiments by Herasymenko (*loc. cit.*), for which the above relation holds, are therefore of a different character from ours.

7. Solutions containing relatively large amounts of alkali salts require high *C.D.*'s to establish constant overvoltages by the commutator method, and the results are similar in character to those obtained in alkaline solution. Here, doubtless, local changes of composition are operative. Where our results for antimony cathodes cover ground already explored for lead and mercury by Glasstone (*loc. cit.*), they are in general agreement with his.

8. No results of a general nature could be obtained connecting the production of stibine in acid solution with overpotential. The yields were small and appeared to depend largely on the solubility of the cathode in the electrolyte, and on extremely high values of *C.D.*

9. In alkaline solution, the overvoltage–current density curves obtained by the direct method show an arrest or inflexion which usually takes place at a voltage not far removed from the maximum given by the commutator method. The decay curves representing the overvoltage at successive short intervals after breaking the current also give indications of this same value, for they sink to, and become constant for a considerable time at, a potential not far removed from it.

10. The relation $\omega + 2h = c$, previously proposed by Sand and Weeks, could not be confirmed with any degree of accuracy, but the results suggest the probability that a relation of the kind may exist which is vitiated by secondary interfering influences.

11. The formation of stibine appears to proceed somewhat more readily in alkaline than in acid solution, and the conditions favourable to it are similar in the two cases. To obtain appreciable yields of the gas, however, it is necessary to blow a rapid current of hydrogen past the electrode, in order to carry away the nascent gas before it has been decomposed by the alkaline solution. The decomposition product formed, when this is not done, has the properties of metallic antimony.

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SIR JOHN CASS TECHNICAL INSTITUTE,
E.C. 3. [*Received, October 22nd*, 1926.]

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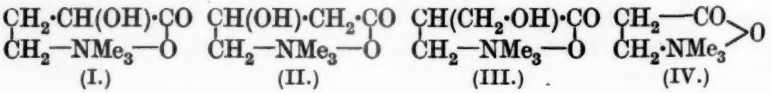
## LIX.—*The Constitution of Carnitine. Part I. The Synthesis of α-Hydroxy-γ-butyrotrimethylbetaine.*

By JOHN WILLIAM CROOM CRAWFORD and JOSEPH KENYON.

IN spite of several investigations the constitution of carnitine, a constituent of muscular tissue, remains unsettled. Two formulæ (I and II) put forward by Krimberg (*Z. physiol. Chem.*, 1907, **53**, 525) represent carnitine as α(or β)-hydroxy-γ-butyrotrimethylbetaine, of which the latter was preferred because of the appearance of β-hydroxy-*n*-butyric acid in the animal organism (*ibid.*, 1908, **56**, 417). A third formula (III) was subsequently advanced by Engeland (*Ber.*, 1921, **54**, 2208) in which carnitine is represented as β′-hydroxy-β-*iso*butyrotrimethylbetaine.




(I.) (II.) (III.) (IV.)

The evidence in support of (I) is that carnitine on oxidation with calcium permanganate yields β-homobetaine (IV) (Engeland, *Ber.*, 1909, **42**, 2457) and on distillation with aqueous baryta gives trimethylamine and crotonic and succinic acids: the production of these two acids is explained by the simultaneous oxidation and reduction of αγ-dihydroxy-*n*-butyric acid, which might be expected to be produced when trimethylamine is eliminated from the carnitine molecule. In favour of (II) is the fact that carnitine, when heated with sulphuric acid at 130°, loses a molecular proportion of water to yield an unsaturated betaine—"*apo*carnitine"—which is reduced by hydrogen in the presence of palladium to γ-butyrotrimethylbetaine (Engeland, *Ber.*, 1921, **54**, 2208). This point, however, does not appear to be well established, as the following data indicate. The reduction product of *apo*carnitine gave a chloroaurate, m. p. 201—203°. On the other hand, the synthetic γ-butyrotrimethylbetaine prepared by Willstätter's method (*Ber.*, 1902, **35**, 617) by Krimberg (*loc. cit.*) gave a chloroaurate of which the highest value of the m. p. was 182—184°.

There does not appear to be any direct experimental evidence in favour of (III): it was advanced as an alternative when Engeland (*loc. cit.*) found that the α-hydroxy-γ-butyrotrimethylbetaine synthesised by the method of Fischer and Göddertz (*vide infra*) was unaffected by hot sulphuric acid under conditions which bring about the dehydration of carnitine.

Moreover, β-hydroxy-γ-butyrotrimethylbetaine has been synthesised by Rollett (*Z. physiol. Chem.*, 1910, **69**, 60), by Engeland (*Ber.*, 1910, **43**, 2705) and by Tomita (*Z. physiol. Chem.*, 1923, **124**, 253), and Engeland states that the properties of his synthetic betaine differed considerably from those of natural carnitine.

α-Hydroxy-γ-butyrotrimethylbetaine has been synthesised by Fischer and Göddertz (*Ber.*, 1910, **43**, 3278) as follows: α-Bromo-γ-phthalimido-*n*-butyric acid was heated with chalk and water, and the resulting hydroxy-derivative hydrolysed with hydrochloric acid to give γ-amino-α-hydroxy-*n*-butyric acid which, by treatment with alcoholic potassium hydroxide and methyl iodide, yielded α-hydroxy-γ-butyrotrimethylbetaine. The validity of this synthesis has been questioned by Engeland (*Ber.*, 1921, **54**, 2208) on the ground that it was shown by Berlin (*Z. Biol.*, 1907, **53**, 514) that, when phthal-β-bromo-*n*-propylimide is hydrolysed by the method described above, it yields, not only the expected β-aminopropyl alcohol, but also α-aminopropyl alcohol as the result of a molecular rearrangement.

It was therefore decided to undertake the synthesis of α-hydroxy-γ-butyrotrimethylbetaine by an alternative method and to ascer-

tain whether the properties of the product thus obtained agreed with those of (*a*) the synthetic betaine of Fischer and Göddertz, (*b*) natural carnitine.

The outline of the synthesis is as follows : β-Chloropropaldehyde diethylacetal, prepared by the action of alcoholic hydrogen chloride on acraldehyde, was hydrolysed by water, and the resulting β-chloropropaldehyde converted into its potassium bisulphite compound; the latter, by the action of potassium cyanide, gave *γ-chloro-α-hydroxy*-n-*butyronitrile* (V), which in turn gave, by the addition of trimethylamine, the *methochloride* of γ-dimethylamino-α-hydroxy-*n*-butyronitrile (VI). On hydrolysis with hydrochloric acid, this nitrile gave the *hydrochloride* of α-hydroxy-γ-butyrotrimethylbetaine (VII).

| | | |
|---|---|---|
| $CH_2Cl$ | $CH_2 \cdot NMe_3Cl$ | $CH_2 \cdot NMe_3Cl$ |
| $CH_2$ | $CH_2$ | $CH_2$ |
| $CH(OH) \cdot CN$ | $CH(OH) \cdot CN$ | $CH(OH) \cdot CO_2H$ |
| (V.) | (VI.) | (VII.) |

The properties of the compound thus obtained agree with those given by Fischer and Göddertz for their synthetic betaine; there can be little doubt, therefore, that the betaine obtained by these authors and that described in this communication are both α-hydroxy-γ-butyrotrimethylbetaine, and that, in consequence, the doubts of Engeland are not justified.

Although Fischer and Göddertz (*loc. cit.*) state that the m. p.'s of several derivatives of their synthetic betaine differ considerably from those of corresponding derivatives of natural *l*-carnitine [according to Kutscher (private communication to Engeland, *Ber.*, 1921, **54**, 2208), carnitine can be racemised by a method which was not described, and the chloroaurate of the racemised compound has the same melting point as that of the chloroaurate of the optically active base], it was decided to attempt the resolution of the synthetic α-hydroxy-γ-butyrotrimethylbetaine in order to prepare crystalline derivatives of its optically active modifications, but unfortunately the attempt was not successful. This drawback is, however, not so serious as was at first thought, since it was found that, contrary to the statement of Engeland (*loc. cit.*), the synthetic α-hydroxy-γ-butyrotrimethylbetaine is decomposed by sulphuric acid at temperatures up to 130° with the production of carbon monoxide—a behaviour quite different from that of carnitine with the same reagent. It is thus definitely established that carnitine cannot be α-hydroxy-γ-butyrotrimethylbetaine.

It is hoped to describe in a further communication the synthesis of β′-hydroxy-β-*iso*butyrotrimethylbetaine.

## EXPERIMENTAL.

Large quantities of acraldehyde were readily prepared by Moureu's method (*Ann. Chim.*, 1921, **15**, 158).

The method of preparing β-chloropropaldehyde diethylacetal described by Wohl and Emmerich (*Ber.*, 1898, **31**, 1797; 1900, **33**, 2761) having given only about 17% of purified material, the following procedure, which was found after many trials to give the best results, was adopted. Dry hydrogen chloride was passed into a mechanically stirred solution of dry calcium chloride (400 g.) and acraldehyde (1000 g.) in 96% alcohol (2000 g.) at such a rate that saturation was reached in 8—10 hours, the reaction mixture being protected from moisture and being kept cold by means of ice. During the addition of hydrogen chloride, the separation of crystalline hydrated calcium chloride was continuous. Next day the liquid portion, consisting of a small upper layer of aqueous-alcoholic calcium chloride solution superimposed on the crude acetal, was filtered or decanted from the solid calcium chloride, and the latter was washed with ether, which was then added to the liquid portion. This was neutralised by adding it drop by drop to a slight excess of cold, well-agitated 10% sodium hydroxide solution. The lime which had separated during the neutralisation was dissolved by the cautious addition of acetic acid, after which the layer of acetal separated quite readily. The aqueous layer was removed, and the acetal was washed with water, then with very dilute sodium hydroxide solution to render it alkaline once more, and finally with water. After drying with calcium chloride, 1653 g. of acetal, b. p. 72—76°/20 mm., were obtained. Yield 56·4%. On redistillation, the product came over almost completely at 74°/20 mm. and had $d_4^{18·7°}$ 0·9951, $d_4^{22·3°}$ 0·9845, $n_D^{18·7°}$ 1·4206, $n_D^{22·3°}$ 1·4203; $[R_L]_D^{18·7°}$ 42·31, $[R_L]_D^{22·3°}$ 42·84 (calc., 42·58).

When the dry hydrogen chloride was passed more rapidly (during 3—4 hours) into the solution, the yield of acetal fell to 48%.

The *potassium bisulphite compound of β-chloropropaldehyde* was prepared by heating under reflux on a water-bath a mixture of β-chloropropaldehyde diethylacetal (666 g.) and water (72 g.; 2 mols.), with frequent shaking until reaction set in; this became apparent by the coalescence of the two liquid layers and the simultaneous refluxing of alcohol. The quickly cooled reaction liquid was vigorously shaken with a concentrated solution of potassium bisulphite (1·1 mols.), the mixture separated, and the unhydrolysed acetal (about 450 g.) reheated with water. This procedure was repeated four times; the amount of unhydrolysed acetal then amounted to only about 5 g. The potassium bisulphite compound

was precipitated in soft, white crystals on addition of alcohol (Found : K, 18·4. Calc. : K, 18·4%). The corresponding sodium bisulphite compound forms nacreous plates (Found : Na, 11·8. Calc. : Na, 11·7%). For the preparation of γ-chloro-α-hydroxy-*n*-butyronitrile, however, it is unnecessary to isolate the solid bisulphite compound : the solution was used direct.

*γ-Chloro-α-hydroxy*-n-*butyronitrile* (V) was prepared by adding during ½ hour a cold aqueous solution of potassium cyanide (400 g. of 92%) to a well-stirred solution of the bisulphite compound, kept below 20°. The upper layer of nitrile was separated, the aqueous portion extracted with ether, and the mixture of nitrile and ethereal extract washed with very dilute acid, dried with sodium sulphate and distilled. The *nitrile* distilled at 91·5°/3 mm. (yield, 316 g.; 66%). It is a colourless, odourless, slightly viscous liquid which can be distilled only at low pressures; $d_4^{19\cdot1°}$ 1·0795, $d_4^{23\cdot1°}$ 1·0765, $n_D^{19\cdot1°}$ 1·4399, $n_D^{23\cdot1°}$ 1·4387 (Found : N, 11·7. $C_4H_6ONCl$ requires N, 11·7%).

*γ-Chloro-α-cyanopropyl benzoate*, prepared by the interaction of γ-chloro-α-hydroxy-*n*-butyronitrile (24 g.), pyridine (17 g.), and benzoyl chloride (29 g.) in ethereal solution, distilled at 147°/3—4 mm. to give a colourless, viscous, highly refractive liquid which soon solidified (yield, 35 g.; 82%). Recrystallised from light petroleum (400 c.c.), it formed small, soft needles, m. p. 59° (Found : N, 6·4. $C_{11}H_{10}O_2NCl$ requires N, 6·3%). The *acetate*, obtained in a similar manner or by the action of boiling acetic anhydride (1 mol.), has b. p. 116—117°/11 mm. and is an odourless, fairly mobile liquid heavier than water; $n_{5790}^{20\cdot1°}$ 1·4342, $n_{5461}^{20\cdot1°}$ 1·4355, $n_{4359}^{20\cdot1°}$ 1·4433 (Found : N, 8·8. $C_6H_8O_2NCl$ requires N, 8·7%).

*γ-Dimethylamino-α-hydroxy*-n-*butyronitrile Methochloride* (VI).—γ-Chloro-α-hydroxy-*n*-butyronitrile (100 g.) was added to a well-stirred solution of trimethylamine (55 g.) in dry amyl alcohol (200 g.), and the mixture maintained at 35—40°; fine crystals of the *amino-nitrile methochloride* were rapidly deposited. After being stirred for several hours, the mixture was cooled and filtered, and the crystalline material washed with dry ether : the amyl alcohol-ether filtrate deposited a second crop of the methochloride, which was removed and washed. Some uncombined γ-chloro-α-hydroxy-*n*-butyronitrile was recovered after the amyl-alcoholic filtrate had been washed with dilute hydrochloric acid to remove trimethylamine and distilled in a vacuum. The methochloride (yield 75—85%) was recrystallised from amyl alcohol (temperature not above 95°) or precipitated from its solution in absolute alcohol by addition of dry ether and was thus obtained in small, glistening, transparent, very hygroscopic plates, m. p. 137°. It is insoluble in

chloroform, benzene, ether, or acetone (Found : N, 15·6. $C_7H_{15}ON_2Cl$ requires N, 15·6%).

The *chloroaurate*, prepared in the usual manner, crystallised, on slow cooling of its aqueous solution, in long, hairy, yellow needles, m. p. 95° (Found : Au, 40·9. $C_7H_{15}ON_2Cl_4Au$ requires Au, 40·9%). The *chloroplatinate* crystallises from aqueous alcohol in radiating clusters of short, slender, orange needles, m. p. 239—240° (decomp.) (Found : Pt, 28·2. $C_{14}H_{30}O_2N_4Cl_6Pt$ requires Pt, 28·1%).

*α-Hydroxy-γ-butyrotrimethylbetaine Hydrochloride* (VII).—A mixture of γ-dimethylamino-α-hydroxy-*n*-butyronitrile methochloride (225 g.), water (270 c.c.), and hydrochloric acid (270 c.c.; 2 mols.) was gently boiled for 2 hours, water being added from time to time to keep the volume of the solution constant. The solution was then evaporated until of syrupy consistency and dried in a vacuum until completely solid. The dry material was heated under reflux with alcoholic hydrogen chloride (275 g. of 10%) for 4 hours. After 12 hours, the ammonium chloride was filtered off and washed with a little absolute alcohol, and the combined filtrate and washings were mixed with an equal volume of water and distilled until the temperature was 95°. The residue was diluted with water, and the solution thus obtained was boiled with charcoal and evaporated until crystallisation set in; the crystalline material was filtered off, and the filtrate again evaporated. The process was repeated several times, the total yield of dry hydrochloride being 234 g. (94%). The betaine hydrochloride crystallises from alcohol in glistening prisms which are not excessively soluble in water, from which it may be crystallised—in marked contrast to the difficultly crystallisable *l*-carnitine hydrochloride.

The chloroaurate produced on mixing concentrated aqueous solutions of the betaine hydrochloride and gold chloride was twice recrystallised from water containing a trace of hydrochloric acid, from which it separated in orange-yellow crystals which, after drying at 105°, melted sharply at 173° without decomposition to give a deep orange-red liquid (Found : Au, 39·3; C, 16·6; H, 4·1; N, 2·9. Calc. for $C_7H_{16}O_3NCl_4Au$ : Au, 39·3; C, 16·8; H, 3·2; N, 2·8%). The melting point was unaltered by further recrystallisation of the material. Fischer and Göddertz (*loc. cit.*) give m. p. 175—176° (corr.) after sintering. Carnitine chloroaurate has m. p. 153—154°.

A *chloroplatinate* was obtained by mixing equivalent quantities of the betaine hydrochloride and chloroplatinic acid in aqueous solution, evaporating the mixture to a syrupy consistency, and adding warm alcohol until the turbidity thus produced was permanent. On cooling, a small amount of oil, which rapidly solidified,

separated along with orange, crystalline plates. These, after recrystallisation from aqueous alcohol, had m. p. 218° (decomp.) after softening at about 196° (Found : Pt, 24·8. $C_{18}H_{40}O_6N_2Cl_6Pt$ requires Pt, 24·75%). The compound is therefore most probably the chloroplatinate of the ethyl ester of α-hydroxy-γ-butyrotrimethylbetaine produced by the action of ethyl alcohol on the free acid.

By the addition of more alcohol to the filtrate, fine, slender, orange needles were obtained. These began to sinter at about 196° and melted at 210—212° (decomp.) (Found : Pt, 26·3. Calc. for $C_{14}H_{32}O_6N_2Cl_6Pt$ : Pt, 26·6%). Fischer and Göddertz (*loc. cit.*) state that the compound prepared by them melts not quite constantly at 216° (corr.) after previous pronounced sintering. They do not, however, give any analytical data. Carnitine chloroplatinate has m. p. 214—218° (decomp.).

In an attempt to effect the resolution of α-hydroxy-γ-butyrotrimethylbetaine the *d*-bromocamphorsulphonate was prepared, but it was a gum which could not be crystallised. The d-*camphorsulphonate* of α-hydroxy-γ-butyrotrimethylbetaine was prepared as follows : The betaine hydrochloride (19·75 g.) and the calculated quantity of the silver salt of Reychler's *d*-camphorsulphonic acid were mixed in aqueous solution, the precipitated silver chloride was removed, the filtrate evaporated, and the resulting syrup kept in a vacuum over sulphuric acid for 2 months. The white, crystalline material obtained separated readily from acetone in tufts of small, slender needles. Repeated crystallisation, however, brought about no alteration in the original rotatory power of the salt.

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## LX.—*Muconic and Hydromuconic Acids. Part IV. Geometrical Form and Reducibility.*

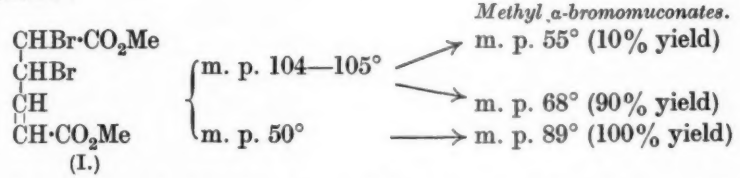
By ERNEST HAROLD FARMER and WALTER MARK DUFFIN.

GEOMETRICAL isomerides of the muconic acid series possess a considerable degree of permanency and can be kept in the light and enter into reaction without change of geometrical form (J., 1923, **123**, 2531). The effect of geometrical form on certain types of molecular reactivity can readily be observed, therefore, and comparison be made with the behaviour of simple ethylenic com-

pounds. In studying the hydrogenation process, twelve compounds of the muconic acid series have been submitted to reduction and every effort has been made to trace variation from the standard type of reduction product.

## I. *Monohalogenated Muconic Esters.*

When *trans-trans*-methyl muconate is treated with bromine, two stereoisomeric bromides (I) are obtained; both of these forms revert to the parent substance on treatment with zinc. On treatment with organic bases, however, each isomeride behaves differently and three monobromomuconic esters are obtained according to the scheme:




(I.)

Careful search for the remaining one of the four theoretically possible isomerides (II), (III), (IV), and (V), in large quantities of material, proved fruitless. Although both the parent dibromides are *racemic* forms, the more fusible (corresponding to the racemic forms in the substituted succinic acids) might be expected to yield the less fusible (*trans-trans-*) methyl bromomuconate, and the less fusible (corresponding to a *meso*-form), the more fusible (geometrically inverted) form of methyl bromomuconate. In the absence of an absolute method of determining geometrical form, use has been made of their capacity for amide formation—a method typical of those used in observing steric effects. If, in the ester–amide transformation, activation preliminary to amide formation be assumed, it would appear to be restricted to the carbalkyloxy-groups acting as self-contained systems; otherwise, according to current conceptions of the activation process in unsaturated chains, the distinction between geometrical forms must disappear.

Each isomeride yielded an amide, two of the forms readily and without degradation, and the third with much greater difficulty and gross decomposition. Derivation, speed of amide formation and solubility being taken into account, the three isomeric methyl α-bromomuconates would seem to be capable of classification as below; since, however, in considering the main product of bromine addition to *trans-trans*-methyl muconate the method of geometrical inversion employed leads to more than one form, of which that regarded as *cis-cis* predominates, it is evident that molecular disturbance has gone too far to allow of the assumption that the

*cis-trans*-form produced is necessarily that isomeride (IV) arising by simple inversion at one double bond.

| | | | |
|---|---|---|---|
| CH——CH<br>X·C·H Br·C·X | CH——CH<br>H·C·X X·C·Br | CH——CH<br>X·C·H X·C·Br | CH——CH<br>H·C·X Br·C·X |
| *trans-trans*<br>m. p. 89° | *cis-cis*<br>m. p. 68° | *cis-trans*<br>m. p. 55° | *cis-trans* |
| (II.) | (III.) | (IV.) | (V.) |

X = $CO_2Me$

Towards reducing agents, the three isomerides behave very differently. The *trans-trans*-form is reduced, on heating for a few minutes with zinc and alcohol, to *trans-trans*-methyl muconate and with zinc and acetic acid to methyl $\Delta^{\beta}$-dihydromuconate. The *cis-cis*-form remains unreduced after prolonged treatment with these reagents, whilst the *cis-trans*-form readily gives an almost quantitative yield of methyl $\Delta^{\beta}$-dihydromuconate after short heating with zinc and acetic acid, although it is not reduced by zinc and alcohol.

If it be taken that the oxygen of the carboxyl group plays an important part in the reduction of such unsaturated compounds, the experimental results are such as might have been expected to arise from the purely steric effect of the geometrical configuration: indeed it would seem that reduction is governed by the accessibility of the carboxyl group. It would appear probable, therefore, that the *cis-trans*-form (IV) was the one actually obtained and investigated and that the alternative form (V), if obtained, would be reducible to methyl muconate by zinc and alcohol.

### II. *Dihalogenated Muconic Esters.*

In this series, the three geometrical forms of ethyl $\alpha\alpha'$-dibromomuconate (*loc. cit.*) have been submitted to reduction. Each of the isomerides was reduced by zinc and acetic acid with such vigour and completeness that discrimination between the isomerides as to reducibility was impossible; the product in each case was ethyl dihydromuconate. A similar result was obtained with the two known forms of ethyl $\alpha\alpha'$-dichloromuconate (*loc. cit.*, p. 2544). There was the interesting result, however, that none of the three dibromo-esters was readily reduced (bromine replaced by hydrogen) with zinc and alcohol. Such a variation from the mode of reactivity of the monobromo-esters probably reflects the difference between a balanced and an unbalanced molecule.

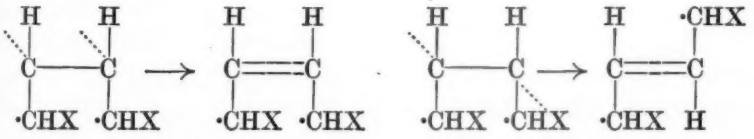
### III. *Muconic Esters.*

Reduction of *trans-trans*- and *cis-cis*-methyl muconate proceeds so slowly with reagents such as zinc and acetic acid that dis-

crimination between their reducibility is impossible. With palladium and hydrogen, both forms are reduced to methyl adipate.

In all the preceding reductions the dihydrogenated product has been of one form (presumably *trans*-) entirely. Thus, almost quantitative yields of ethyl dihydromuconate (m. p. 2°) and methyl dihydromuconate (m. p. 16°) have been obtained repeatedly; no trace of a second form has been recognisable on any occasion. Since numerous attempts to isolate a second geometrical form, including the removal of bromine from the stereoisomeric methyl and ethyl ββ′-dibromoadipates, have been unsuccessful, it appears certain that such a form can only have a very low degree of stability or is incapable of existence.

There appears no very obvious relationship between the geometrical form of the system C:C·C:C and that of its reduction product CH·C:C·CH; this is the case whether the process be represented on the Thiele, the Lowry, or the electronic plan. If represented in the van 't Hoff manner, reduction could yield *cis*- and *trans*-isomerides only by variation in the linking of the free valencies. Thus the two ways (A) and (B) are possible. Where *cis*- and *trans*-forms




(A.) (B.)

are of comparable stability, both isomerides might be expected to arise in the reduction of any one of the isomeric muconic forms. Departure from this equal favouring of *cis*- and *trans*-dispositions (subject to subsequent inversion processes due to experimental conditions) might arise (*a*) by the steric effects of the terminal groups tending towards *trans*-forms, and (*b*) by a tendency towards symmetrical disposition of free valencies as in (B) above, also tending to the production of *trans*-forms. If the effect of terminal addition is gained merely by the occurrence of a secondary effect, a process of molecular rearrangement, then the tendency (probably largely steric) towards stability might be expected to result in the appearance of *trans*-forms. The persistent occurrence of a single form of dihydromuconic ester in the foregoing reductions would seem to be the logical result, were it not for the failure of methods other than reduction to yield the geometrical isomeride. In extending observations to other muconic systems, an instance was discovered in which the form of the reduction product was dependent on that of the parent compound.

### IV. ββ′-*Diphenylmuconic Esters.*

From ethyl *meso*-ββ′-diphenyl-ββ′-dihydroxyadipate Beschke (*Annalen*, 1912, **384**, 143) obtained two diphenyldihydromuconic acids related either as *cis*- and *trans*- or as $\Delta^{\alpha}$- and $\Delta^{\beta}$-isomerides. On re-examination, Beschke's acids proved to be *cis*- and *trans*-forms of the $\Delta^{\beta}$-acid; both yielded benzoylacetic acid as the sole isolable oxidation product when treated with ozone in alkaline solution :

$$HO_2C\cdot CH_2\cdot CPh{:}CPh\cdot CH_2\cdot CO_2H \xrightarrow{O_3} 2COPh\cdot CH_2\cdot CO_2H.$$

The higher-melting acid has the *trans*-configuration, since Beschke showed that this form only could be converted into dihydroxychrysene. In Beschke's synthesis a sodium diphenylmuconate (VIII) was obtained from the dehydration product (VII) of the *meso*-dihydroxy-ester (VI).

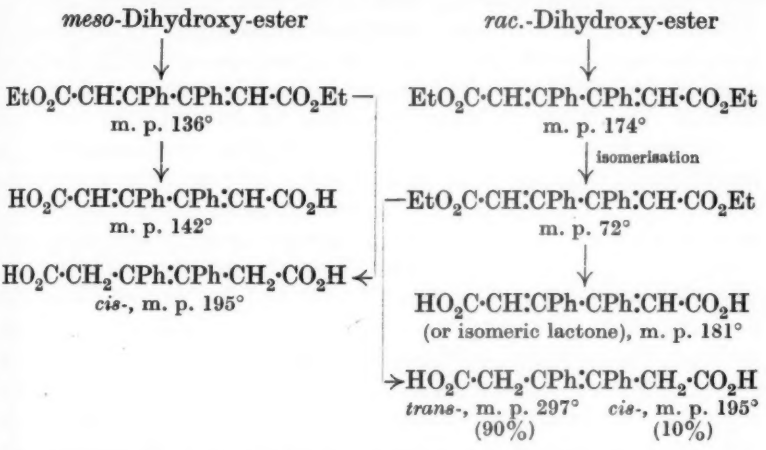
$$\begin{matrix} Ph\cdot C(OH)\cdot CH_2\cdot CO_2Et \\ Ph\cdot C(OH)\cdot CH_2\cdot CO_2Et \end{matrix} \xrightarrow[H_2SO_4]{Ac_2O+} \begin{matrix} PhC\text{——}CPh\cdot CH_2\cdot CO_2Et \\ CH\quad O \\ \quad CO \end{matrix} \xrightarrow{NaOH}$$

(VI.) (VII.)

(VIII.) $\begin{matrix} Ph\cdot C{:}CH\cdot CO_2Na \\ Ph\cdot C{:}CH\cdot CO_2Na \end{matrix}$

This substance reverted to the lactone on acidification, but yielded through the silver salt an ethyl diphenylmuconate, m. p. 72°; reduction with sodium-amalgam gave a mixture of the two dihydro-acids (90% *trans*, 10% *cis*). The genesis of these acids became clearer when both dihydroxy-esters were submitted to dehydration under mild conditions. The two stereoisomerides then yielded different forms of ethyl diphenylmuconate, of which that derived from the *racemic* ester passed spontaneously, on short standing, into a third isomeride which proved to be identical with Beschke's ester. The production of the last from a *meso*-compound must have involved stereoisomeric inversion, due to the somewhat drastic conditions employed. Each of the stable esters yielded a corresponding acid on hydrolysis with sulphuric acid; each gave a characteristic product on reduction with sodium amalgam. Isomeric change of the unstable form was too rapid to allow of its reduction product being differentiated from those of its isomerides. It is impossible from the evidence obtained to assign formulæ to the three ethyl diphenylmuconates produced. All attempts to discover their individual configurations by oxidative processes (compare Behrend and Heyer, *Annalen*, 1919, **418**, 294) were unsuccessful owing to their great resistance to oxidation. It is quite clear, however, that the form of the reduction product has a definite

relation to that of the parent butadiene compound; whether this is a necessary and fundamental result of the mechanism of reduc-




tion or merely a peculiarity arising from the nature of the substituent groups in these substances can only be determined by an examination of other examples. A pronounced steric effect capable of deciding the configuration of the reduction product might be expected to lead to the formation of the same stable reduced form from all the isomeric butadiene esters, not to different forms of comparable stability. On the other hand, it is probable that the spontaneous isomerisation noted above is a volume effect of the kind

$$\begin{matrix} Ph\cdot C- \\ \| \\ EtO_2C\cdot C\cdot H \end{matrix} \longrightarrow \begin{matrix} Ph\cdot C- \\ \| \\ H\cdot C\cdot CO_2Et \end{matrix}$$

rather than the reverse.

## EXPERIMENTAL.

*Methyl Muconate Dibromide.*—The gradual addition of bromine (1 mol.) to *trans-trans*-methyl muconate in chloroform solution in direct sunlight gave a product, isolated by evaporation of the solvent in a vacuum, consisting of two isomeric *dibromides* in the approximate proportion 12 : 1, which were separated by fractional crystallisation from ethyl alcohol or petroleum (b. p. 60—80°). The less soluble, more abundant form crystallised in stout, colourless prisms, m. p. 104—105° (Found: Br, 48·35. $C_8H_{10}O_4Br_2$ requires Br, 48·4%), the more soluble form as a coarse powder, m. p. 50° (Found: Br, 48·4%).

*Isomeric Methyl α-Bromomuconates.*—Dry ethereal solutions of the isomeric dibromides were treated in turn with ethereal diethyl-

amine in slight excess. Diethylamine hydrobromide separated rapidly and quantitatively in each case. The ethereal solutions, freed from base by washing with dilute acid, yielded, on evaporation, colourless oils which solidified completely. The product from the more fusible dibromide was homogeneous; it crystallised from ethyl alcohol or petroleum in long, stout needles, m. p. 89° (Found : Br, 31·95. $C_8H_9O_4Br$ requires Br, 32·1%).

The less fusible dibromide yielded a mixture of isomeric monobromo-esters. These were separated completely only by a prolonged and laborious process of fractional crystallisation, using ethyl alcohol and petroleum (b. p. 60—80°) alternately. The less soluble of these isomerides crystallised from alcohol or petroleum in stout prisms, m. p. 68° (Found : Br, 32·1%); the more soluble crystallised from alcohol in small, compact prisms, m. p. 55° (Found : Br, 31·9%). It is a remarkable fact that, although these isomerides were stable when pure, mixtures of the two lower-melting forms invariably changed in a few days to a viscous, pale yellow oil, no longer crystallisable. Removal of hydrogen bromide from the two methyl muconate dibromides could also be accomplished by the use of excess of hot pyridine or the calculated quantity of cold alcoholic sodium methoxide.

*Formation of Amides from Isomeric Methyl α-Bromomuconates.*—Equal quantities of the three isomerides were treated with excess of concentrated aqueous ammonia at room temperature. The esters gradually dissolved, with the separation of crystalline amides. The approximate times of conversion are shown in the table below:

| Bromo-ester. M. p. | Suggested form. | Comparative solubility in organic solvents. | Time of conversion into amide. | Amide. M. p. |
|---|---|---|---|---|
| 89° | *trans-trans* | Most insoluble | 4 hours (no decomp.) | 235° |
| 68 | *cis-cis* | | 9 hours (gross decomp.) | 197 |
| 55 | *cis-trans* | Most soluble | 2½ hours (no decomp.) | 156 |

The *trans-trans*-amide (m. p. 235°) crystallised from water as a colourless powder (Found : Br, 36·5. $C_6H_7O_2N_2Br$ requires Br, 36·5%); the *cis-cis* (m. p. 197°) in stout prisms (Found : Br, 36·4%); the *cis-trans* in long needles (Found : Br, 36·6%).

*Reduction of Methyl α-Bromomuconates.*—(a) *With zinc and acetic acid.* To the ester, dissolved in glacial acetic acid, excess of zinc dust was added in small quantities. The mixture was heated on a steam-bath for 20 minutes, cooled, poured into water, and filtered. The ethereal extract of the filtrate was freed from acetic acid and dried, and the solvent evaporated.

The *trans-trans*-ester was readily reduced: the product, which solidified on cooling, crystallised from light petroleum in well-formed, colourless prisms, m. p. 16°, which obviously represented only one of the two possible geometrical forms of *methyl* $\Delta^{\beta}$*-dihydromuconate* (Found: C, 55·7; H, 7·0. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). Only the slightest trace of non-crystallisable ester remained in the solvent. Bromination of this ester in chloroform solution gave an almost quantitative yield of the methyl ββ′-dibromoadipate, m. p. 93° (*loc. cit.*, p. 2541). Hydrolysis with dilute sulphuric acid yielded pure $\Delta^{\beta}$-dihydromuconic acid.

The reduction of the *cis-cis*-ester was attempted in a similar fashion. The product after 20 minutes' heating was an oil which did not solidify. On distillation, it was obtained as a colourless oil of boiling point and composition differing little from those of the original compound. Further treatment with zinc and acetic acid for 1 hour yielded a similar oil with a large bromine content. Inability to crystallise these products probably arose from admixture of slight quantities of reduction products; it was frequently found that mixtures of the isomeric bromo-esters with small amounts of impurities could be solidified only with the utmost difficulty.

Reduction of the *cis-trans*-ester to methyl $\Delta^{\beta}$-dihydromuconate, m. p. 16°, proceeded exactly as with the *trans-trans*-form. In this case also, only one geometrical form of the reduced product could be isolated.

(b) *Zinc and alcohol* (*or acetone*). The *trans-trans*-monobromo-ester was refluxed with acetone and excess of zinc dust. Crystals of *trans-trans*-methyl muconate soon separated from the boiling solution. After ½ hour the suspended methyl muconate was redissolved by addition of more acetone, and the resulting solution filtered. The filtrate gave, on evaporation, an almost quantitative yield of methyl muconate, which crystallised from methyl alcohol in the characteristic, long needles, m. p. 156°.

The *cis-cis*-ester was treated similarly, but was recovered unchanged. The bulk of the *cis-trans*-ester was recovered in pure condition after treatment in this way: if any reduction occurred, it was insignificant in extent.

*Reduction of Isomeric Ethyl αα′-Dibromomuconates.*—These substances were prepared as described in Part II of this series (*loc. cit.*). Each of the three isomerides passed almost quantitatively into ethyl dihydromuconate on treatment with zinc and acetic acid as above. A careful examination of the reduction product was made in each case. Hydrolysis with dilute sulphuric acid yielded only $\Delta^{\beta}$-dihydromuconic acid, m. p. 197°, and recrystallisation from light petroleum yielded pure *ethyl* $\Delta^{\beta}$*-dihydromuconate* (presumably

*trans*-) in colourless prisms, m. p. 2° (approx.). From the mother-liquor, only a very small quantity of non-crystallisable ester was obtained. This, on hydrolysis, also yielded dihydromuconic acid, m. p. 197°.

With zinc dust and alcohol (or acetone), no appreciable reduction was effected in ½ hour. Each of the three isomerides was recovered practically quantitatively.

*Reduction of Isomeric Ethyl αα′-Dichloromuconates.*—The two known isomerides (*loc. cit.*, p. 2540) were similarly treated with zinc dust and acetic acid. Rapid and complete reduction to ethyl $\Delta^{\beta}$-dihydromuconate was effected. Again, only one form (m. p. 2° approx.) of this substance could be isolated.

*Reduction of Isomeric Methyl Muconates.*—(a) *With zinc and acetic acid.* Reduction of the two known isomerides (*loc. cit.*, p. 2546) proceeded so slowly with zinc and acetic acid that isomerisation of the lower-melting form probably preceded reduction. The product in each case was methyl $\Delta^{\beta}$-dihydromuconate, m. p. 16°, or the corresponding acid.

(b) *With sodium amalgam.* The reduction of the *trans-trans*-acid (corresponding to the methyl ester, m. p. 156°) has previously been described. The product is entirely $\Delta^{\beta}$-dihydromuconic acid, m. p. 197°. Methyl muconate, m. p. 75°, was hydrolysed with alkali to a mixture of the corresponding acid and lactone (*loc. cit.*, p. 2548), which was reduced in the usual way with sodium amalgam in a current of carbon dioxide. The product yielded ββ′-dihydromuconic acid, m. p. 197°, only.

(c) *With palladium and hydrogen.* The two isomerides yielded methyl adipate when reduced at atmospheric pressure by the method of Skita. Reduction to the dihydro-stage could not be secured by restricting the hydrogen supplied : in this case a portion of the ester remained unreduced.

*Action of Zinc on Isomeric Methyl αα′-Dibromoadipates.*—The two dibromo-esters (*loc. cit.*, p. 2541) were each dissolved in acetone and carefully treated with excess of zinc dust. Reaction, which took place rapidly, was completed by heating for a short time on a steam-bath. The product, isolated in the usual way, was in each case methyl $\Delta^{\beta}$-dihydromuconate, m. p. 16°.

*Ethyl ββ′-Diphenyl-ββ′-dihydroxyadipate.*—The *meso*- and *racemic* forms of this ester were obtained in essentially the way described by Beschke (*loc. cit.*); magnesium, however, was employed instead of zinc, the reaction being started by addition of a crystal of iodine.

*Action of Phosphorus Halides on Dihydroxy-esters.*—Both *meso*- and *racemic* forms yielded, when allowed to stand for 24 hours with the calculated amount (2 mols.) of phosphorus tribromide,

diphenylmuconic esters. Simple replacement of hydroxyl by bromine could not be effected, the bromine content of the product never rising to 1%. The *meso*-ester (m. p. 168°) yielded invariably and solely an *ethyl ββ′-diphenylmuconate* which crystallised from benzene or alcohol in short prisms, m. p. 136° (Found: C, 75·6; H, 6·3. $C_{22}H_{22}O_4$ requires C, 75·5; H, 6·3%). The *racemic* ester (m. p. 137°) similarly yielded a second, more soluble form of the same ester which crystallised from the same solvents in well-defined needles, m. p. 174° (Found: C, 75·6; H, 6·3%).

Treatment of benzene solutions of the hydroxy-esters with phosphorus pentabromide or pentachloride gave similar results. Moderation of the reaction by cooling to 0° did not prevent the removal of hydrogen bromide.

*Isomerisation of Ethyl Diphenylmuconate*, m. p. 174°.—The pure dry ester, when allowed to stand in the air for 15 minutes, became sticky. Recrystallisation at this stage yielded a mixture of ethyl diphenylmuconates, m. p.'s 174° and 72°. When the sticky mass was allowed to stand longer (45 minutes), it set to a glassy solid which crystallised from alcohol in small needles, m. p. 72° (Found: C, 75·55; H, 6·3%). Yield 95%. The rapid isomerisation of the form, m. p. 174°, prevented satisfactory observations of the geometrical form of its reduction product.

*Preparation of Isomeric Ethyl ββ′-Diphenylmuconates.*—For the preparation of considerable quantities of these esters the phosphorus halide method was inconvenient. The following methods were therefore employed.

(*a*) The dihydroxy-ester was refluxed with zinc dust (3 parts) and absolute alcohol (8—10 parts) for 6 hours. In the case of the *meso*-ester, crystallisation of ethyl diphenylmuconate (m. p. 136°) from the hot filtered solution commenced at once; with the *racemic* ester, concentration was necessary before the unstable form (m. p. 174°) separated. This process gave excellent results with the pure dihydroxy-esters.

(*b*) The dihydroxy-ester was boiled for 1 hour with acetic anhydride and the product was cooled and extracted with petroleum (b. p. 80—100°) (in which acetic anhydride is not very soluble). Evaporation of the solvent and cooling of the residue to 0° caused crystallisation of the dehydrated ester. This method was usually employed for treating the residual sludge of the "Reformatski" product. This contained a considerable quantity of difficultly recoverable *racemic* ester which yielded directly, on dehydration for 24 hours, a crystalline product purifiable by one recrystallisation.

*ββ′-Diphenylmuconic Acid.*—Hydrolysis of ethyl diphenylmuconate, m. p. 136°, with dilute sulphuric acid yielded the corresponding

acid, which separated from alcohol as a white, crystalline powder, m. p. 142° [Found: C, 73·1; H, 4·7; *M* (dibasic), 298. $C_{18}H_{14}O_4$ requires C, 73·5; H, 4·7%; *M*, 294]. The isomeric ester, m. p. 72°, yielded, on similar treatment, an acid, m. p. 181°. This also separated from alcohol as a white, crystalline powder (Found: C, 73·6; H, 4·7%; equiv., 221) and was probably identical with Beschke's 2 : 3-diphenylcrotonolactone-3-acetic acid.

*Reduction of Isomeric Ethyl Diphenylmuconates.*—The two stable esters were separately hydrolysed by adding a hot aqueous solution of caustic soda to a boiling alcoholic solution of the ester until permanent alkalinity was secured. After the alcoholic liquor had been boiled for 1 hour, the precipitated sodium salt was filtered off and dissolved in a small quantity of water. Gradual addition of 3% sodium amalgam until effervescence ceased, followed by filtration and acidification, gave an immediate precipitate of the reduced acid. cis-ββ′-*Diphenyl*-$\Delta^{\beta}$-*dihydromuconic acid*, the sole product from ethyl diphenylmuconate (m. p. 136°), crystallised from water in colourless prisms, m. p. 195° (Found: C, 72·9; H, 5·2. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·3%). trans-ββ′-*Diphenyl*-$\Delta^{\beta}$-*dihydromuconic acid*, which was produced together with its isomeride from ethyl diphenylmuconate (m. p. 72°), crystallised from alcohol in colourless prisms, m. p. 297° (Found: C, 72·9; H, 5·3%). The *ethyl* esters of the *cis*- and *trans*-acids, obtained by saturating alcoholic solutions with hydrogen chloride, crystallised from alcohol in colourless prisms, m. p. 56° and 86°, respectively.

*Oxidation of* $\Delta^{\beta}$-*Diphenyldihydromuconic Acids.*—Each of the acids (3 g.) was separately dissolved in a slight excess of dilute sodium carbonate solution and treated with a rapid current of ozonised oxygen for 48 hours. After air had been bubbled through the brown liquids to remove dissolved ozone, the products were acidified and extracted with ether. The ethereal extract contained in each case a mixture of unchanged acid and benzoylacetic acid, which were separated by fractional crystallisation from benzene and petroleum. The benzoylacetic acid derived from each acid, after the final crystallisation from alcohol, melted and decomposed at 103—104° and gave a violet-red coloration with ferric chloride (Found: C, 65·7; H, 4·9. Calc.: C, 65·8; H, 4·9%).

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# LXI.—*The Reaction between Grignard Reagents and 10-Chlorophenoxarsine or 10-Chloro-5 : 10-dihydrophenarsazine.*

By JOHN ALFRED AESCHLIMANN.

THE method of preparing 10-ethylphenoxarsine by heating 10-chlorophenoxarsine with magnesium ethyl bromide described by the author (J., 1925, **127**, 813) has been extended to the 10-*methyl* and 10-*phenyl* compounds, derivatives of which have been prepared. 10-Methylphenoxarsine can be readily obtained by performing the Grignard reaction in the cold as described by Roberts and Turner (J., 1926, 1210), who, although they did not isolate any arsine, claimed that their method is of general application. That this is not the case follows from the experimental results described below, and agrees with the previous work of Lewis, Lowry, and Bergheim (*J. Amer. Chem. Soc.*, 1921, **43**, 890), who failed to isolate either the phenyl- or the ethyl-phenoxarsine under similar conditions, but mistook for the latter a compound, m. p. 218°, which was probably phenoxarsinic acid, m. p. 219°, as this can be isolated by allowing the oxide formed in the reaction to oxidise in air. Of the above three arsines, only the phenyl derivative is crystalline.

In several attempts to obtain 10-phenylphenoxarsine by the condensation of diphenyl ether with phenyldichloroarsine in presence of aluminium chloride, only 10-chlorophenoxarsine was obtained. This result is analogous to that obtained by Burton and Gibson (J., 1926, 465) in the condensation of diphenylamine and phenyldichloroarsine, although they used no catalyst to facilitate the decomposition of the dichloroarsine to arsenious chloride. 10-Chlorophenoxarsine does not give 10-phenylphenoxarsine on being heated with benzene and aluminium chloride.

10-Chloro-5 : 10-dihydrophenarsazine reacts with two molecules of the respective Grignard reagents to give 10-*methyl*-5 : 10-*dihydrophenarsazine*, 10-*ethyl*-5 : 10-*dihydrophenarsazine*, and 10-*phenyl*-5 : 10-*dihydrophenarsazine*, hydrocarbons also being formed owing to the presence of the NH-group. When the reaction mixture is cooled during addition of the chloroarsine, the formation of hydrocarbon does not take place and the heavy oil which separates from the ethereal solution should contain the : NH(MgI)R group. Treatment of this with methyl iodide, however, does not produce 5 : 10-dimethyl-5 : 10-dihydrophenarsazine, but 10 : 10-*dimethyl*-5 : 10-*dihydrophenoxarsonium iodide*, which is also the product when the methylation of 10-methyl-5 : 10-dihydrophenarsazine is attempted

under various conditions. The latter compound, unlike 10-chloro-5 : 10-dihydrophenarsazine (Wieland and Rheinheimer, *Annalen*, 1921, **423**, 1), which loses hydrogen chloride from the 5 : 10-positions to produce phenarsazine when heated in a vacuum, loses methyl iodide under these conditions and re-forms 10-methyl-5 : 10-dihydrophenarsazine. The methyldihydrophenarsazine combines with ethyl iodide, and the ethyldihydrophenarsazine with methyl iodide, to form the same 10-*methyl* : 10-*ethyl*-5 : 10-*dihydrophenarsazonium iodide*. The formation of the arsonium rather than the ammonium compound by addition of alkyl iodide recalls the ease of formation of sulphonium compounds from the similarly constituted di-*p*-nitrodiphenylamine sulphoxide (Smiles and Hilditch, J., 1908, **93**, 145, 1687).

The observation of Turner, Sheppard, and Bolton (J., 1925, **127**, 547), that diphenylene disulphide is formed when a mixture of arsenic trichloride and diphenyl sulphide is heated with aluminium chloride, has been extended to the reaction between arsenic trichloride or phenyldichloroarsine and the double compound $(C_6H_5)_2S,AlCl_3$ (Böeseken, *Rec. trav. chim.*, 1905, **24**, 219). Equimolecular quantities of triphenylarsine, sulphur monochloride, and aluminium chloride similarly fail to produce a cyclic arsine, the product after treatment with water being triphenylarsine dihydroxide.

## Experimental.

10-Methyl- and 10-ethyl-phenoxarsines were each prepared by the addition of 10-chlorophenoxarsine (10 g.) to the stirred Grignard reagent (2 mols.). The yields obtained after decomposition of the products as described by Roberts and Turner (*loc. cit.*) were: from MgMeI, 85%; from MgEtI, 40% (impure); from MgEtBr, 20% (impure). 10-Phenylphenoxarsine was not isolated in this way, as it was difficult to separate from unchanged chlorophenoxarsine.

10-Ethylphenoxarsine was obtained in 80% yield by heating 10 g. of 10-chlorophenoxarsine in 60 c.c. of benzene with 1½ mols. of magnesium ethyl bromide in 50 c.c. of ether for 2½ hours. When only 1¼ mols. of the Grignard reagent were used as previously described, the yield was about 70%.

10-*Methylphenoxarsine* is a colourless oil, b. p. 185°/20 mm., 198—200°/40 mm. (Found: C, 60·7; H, 4·2. $C_{13}H_{11}OAs$ requires C, 60·5; H, 4·3%).

10-*Methylphenoxarsine dihydroxide*, m. p. 94°, was obtained by dissolving the arsine in excess of hydrogen peroxide solution, evaporating the water and recrystallising the residue from benzene (Found: C, 53·7; H, 4·45. $C_{13}H_{13}O_3As$ requires C, 53·4; H, 4·45%).

It is dehydrated to the oxide when heated in a vacuum at 50° (Found : loss, 5·9. Calc. for 1 $H_2O$; loss, 6·1%). The hydroxide is re-formed after 12 hours' exposure of the oxide to air.

10 : 10-Dimethylphenoxarsonium iodide forms white needles which melt at 225° when slowly heated and at 220° when rapidly heated in closed or in open tubes [Found : I (Carius), 31·7. Calc. : I, 31·7%]. Roberts and Turner (*loc. cit.*) give m. p. 207°.

10-Methyl-10-ethylphenoxarsonium iodide (Aeschlimann, *loc. cit.*) is less readily formed from 10-methyl- than from 10-ethyl-phenoxarsine and the requisite alkyl iodide. Only the white compound was isolated in the former case.

10-*Methyl*-10-*carboxymethylphenoxarsonium bromide*, m. p. 199°, was formed on heating equimolecular quantities of 10-methyl-phenoxarsine and bromoacetic acid for 15 minutes at 90°, the stirred mixture gradually becoming solid. The product was washed with ether and recrystallised from alcohol, in which it was not easily soluble (Found : Br, 20·3, 20·6; equiv. by titration with alkali, 394. $C_{15}H_{14}O_3BrAs$ requires Br, 20·2%; equiv., 397).

10-*Ethylphenoxarsine sulphide* was slowly formed by the action of hydrogen sulphide on an aqueous solution of the oxide, or by addition of excess of sulphur to a solution of 10-ethylphenoxarsine in carbon disulphide. It is soluble in ether, and crystallises from alcohol in long needles, m. p. 109° (Found : S, 10·1. $C_{14}H_{13}OSAs$ requires S, 10·6%).

10-*Phenylphenoxarsine* was obtained in 75% yield by heating the Grignard reagent prepared from 15 g. of bromobenzene with 10 g. of 10-chlorophenoxarsine in benzene for 4 hours. (The reaction is incomplete after 2½ hours' heating, and the unchanged chloroarsine is difficult to remove from the product, which boils at 270°/30 mm. and solidifies slowly.) It crystallised from alcohol in colourless needles, m. p. 107° (Found : C, 66·8; H, 4·1. $C_{18}H_{13}OAs$ requires C, 67·5; H, 4·1%).

10-*Phenyl*-10-*methylphenoxarsonium iodide*, m. p. 175°, did not appear to be formed until the reactants were heated (Found : I, 27·6. $C_{19}H_{16}OIAs$ requires I, 27·5%).

10-*Phenylphenoxarsine oxide*, m. p. 184°, was formed by dehydrating the hydroxide in a vacuum at 50° (Found : C, 64·2; H, 3·8. $C_{18}H_{13}O_2As$ requires C, 64·4; H, 3·9%). The hydroxide was obtained by the action of hydrogen peroxide, or of sulphur monochloride and water (Zuckerkandl and Sinai, *Ber.*, 1921, **54**, 2484), on 10-phenylphenoxarsine. It is deliquescent, and retains 1½ mols. of water on drying to constant weight in a desiccator; it then melts at 93° (Found : loss on conversion into oxide, 7·2. Calc. for $1\frac{1}{2}H_2O$ : loss, 7·4%).

10-*Methyl*-5 : 10-*dihydrophenarsazine* was obtained by the addition of 14 g. of powdered 10-chloro-5 : 10-dihydrophenarsazine in three portions to the Grignard reagent (2·1 mols.) prepared from 16 g. of methyl iodide and 2·6 g. of magnesium in 50 c.c. of ether. (Usually ebullition and evolution of hydrocarbon vapours were allowed to occur, and immediate solution then took place. If, however, the reagent was cooled in a freezing mixture during the addition, gas was not evolved and two layers were formed. When this mixture was heated with methyl iodide, only the arsonium iodide and the methyl arsine were formed.) The mixture was heated for a short time to complete the reaction and then decomposed in the usual manner; the residue crystallised after evaporation of the ether from the extract. After recrystallisation from hot alcohol, the *dihydrophenarsazine* melted at 105°, and was soluble in the usual solvents except light petroleum. It was usually yellow, but formed almost colourless plates after being recrystallised several times (Found : C, 60·6; H, 4·0. $C_{13}H_{12}NAs$ requires C, 60·7; H, 4·1%).

10-*Ethyl*-5 : 10-*dihydrophenarsazine*, obtained in a similar way, melted at 75° (Found : C, 62·0; H, 5·0. $C_{14}H_{14}NAs$ requires C, 62·0; H, 5·2%).

10-*Phenyl*-5 : 10-*dihydrophenarsazine*, m. p. 142°, was less soluble in alcohol than the alkyldihydrophenarsazines, and required heating for its formation (Found : C, 68·1; H, 4·4. $C_{18}H_{14}NAs$ requires C, 67·7; H, 4·4%).

All three arsines reacted with methyl iodide to form arsonium iodides, crystallisable from hot alcohol and only slightly soluble in water. The methyl compound reacted in the cold, the others required heating. Even in presence of a large excess of methyl iodide in a sealed tube at 100°, only one molecule of the iodide took part in the reaction; a similar combination took place at the ordinary temperature.

10 : 10-*Dimethyl*-5 : 10-*dihydrophenarsazonium iodide* has m. p. 259° (slow heating), 268° (rapid heating) (Found : C, 42·1; H, 3·6; I, 31·7. $C_{14}H_{15}NIAs$ requires C, 42·2; H, 3·8; I, 32·0%).

10-*Methyl*-10-*ethyl*-5 : 10-*dihydrophenarsazonium iodide*, m. p. 236° (rapid heating), 229° (slow heating), was obtained from either the methyl or the ethyl compound and the appropriate alkyl iodide (Found : I, 30·4. $C_{15}H_{17}NIAs$ requires I, 30·7%).

10-*Phenyl*-10-*methyl*-5 : 10 *dihydrophenarsazonium iodide* has m. p. 158° (decomp.) (Found : I, 27·9. $C_{19}H_{17}NIAs$ requires I, 27·6%).

5-*Acetyl*-10-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 154°, was obtained by boiling the arsazine with an excess of acetic anhydride for 1 hour, removing the latter in a vacuum, and crystallising the

product from alcohol. It is less soluble in ether than the arsazine (Found : C, 60·6; H, 4·5. $C_{15}H_{14}ONAs$ requires C, 60·2; H, 4·7%).

In conclusion, I express my thanks to the authorities of the Chemical Departments at Battersea Polytechnic and Cambridge University for providing the necessary facilities for this research.

UNIVERSITY CHEMICAL LABORATORIES, CAMBRIDGE. BATTERSEA POLYTECHNIC, S.W.11.

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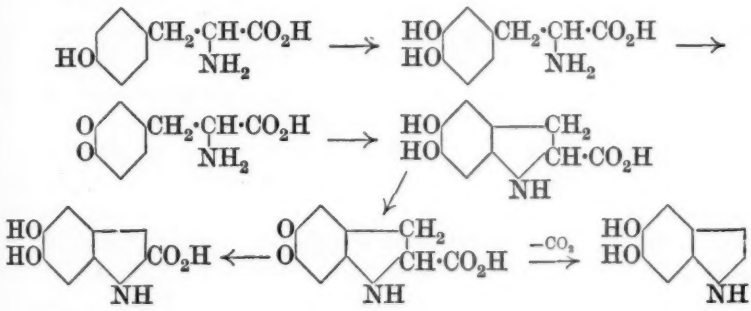
## LXII.—*Synthesis of* 5 : 6-*Dimethoxyindole and its* 2-*Carboxylic Acid.*

By ALBERT EDWARD OXFORD and HENRY STANLEY RAPER.

IT has been recently shown by Raper (*Biochem. J.*, in the press) that when tyrosine is oxidised by the enzyme tyrosinase, a series of changes occurs which results in the production of 5 : 6-dihydroxyindole and to a lesser extent of 5 : 6-dihydroxyindole-2-carboxylic acid. These changes, which represent a new type of indole synthesis, are as follows :

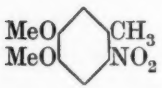


Both 5 : 6-dihydroxyindole and its 2-carboxylic acid are very easily oxidised and can only be isolated as dimethoxy-compounds by methylation in a neutral atmosphere. For purposes of identification, it was necessary to synthesise them, since they had not been previously prepared. Perkin and Rubenstein (J., 1926, 357) have described a synthesis of ethyl 5 : 6-dimethoxyindole-2-carboxylate, but the yields were poor and the ester was not easily converted into the free acid because the latter tended to produce tarry products on heating in the presence of acids.

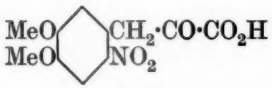
Attempts to obtain 5 : 6-dimethoxyindole by condensing *as*-dichlorodiethyl ether with 4-aminoveratrole (compare Berlinerblau, *Monatsh.*, 1887, **8**, 180) proved fruitless. The method finally

adopted was that used by Blaikie and Perkin (J., 1924, **125**, 296) in the preparation of certain of the monomethoxyindoles.

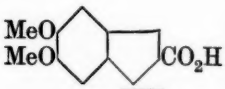
6-Nitrohomoveratrole (I), when condensed with ethyl oxalate in the presence of potassium ethoxide, yields 2-nitro-4 : 5-dimethoxyphenylpyruvic acid (II), from which 5 : 6-dimethoxyindole-2-carboxylic acid (III) is obtained by reduction with ferrous sulphate and ammonia.




(I.)




(II.)




(III.)

The last-named acid loses carbon dioxide at its melting point, yielding 5 : 6-dimethoxyindole.

The series of changes described above which tyrosine undergoes as a result of the action of the enzyme tyrosinase is completed by the formation of a black, insoluble pigment—melanin. This is produced undoubtedly by the oxidation in air of 5 : 6-dihydroxyindole. Similar pigments are produced in nature, both in animals and in plants, and they are known to contain within their molecule some cyclic structure in which nitrogen is present. The production of dihydroxyindole from tyrosine indicates, therefore, that the nitrogen-containing cyclic structure is present before melanin is formed and suggests that tyrosine and not tryptophan may be the chief mother-substance of melanin pigments in nature.

The first stage of the oxidation brought about by the enzyme, *i.e.*, the production of 3 : 4-dihydroxyphenylalanine from tyrosine, is of considerable interest in that it shows a possible method by which certain pyrocatechol derivatives may arise in nature. The 3 : 4-dihydroxy-grouping—often methylated—is of relatively frequent occurrence, *e.g.*, in adrenaline, 3 : 4-dihydroxyphenylalanine, vanillin, eugenol and other naturally occurring products.

## Experimental.

*2-Nitro-4 : 5-dimethoxyphenylpyruvic Acid* (II).—Potassium (9·9 g.) was pulverised under boiling benzene (250 c.c.). After the liquid had been allowed to cool, and ether (250 c.c., dry and free from alcohol) had been added, a solution of 100% alcohol (14·5 c.c.) in dry ether (15 c.c.) was slowly run in with shaking, after which the mixture was kept for ½ hour. Ethyl oxalate (37·2 g.) was now added followed by a solution of 6-nitrohomoveratrole (50 g.) in dry benzene (300 c.c.). The mixture, protected from atmospheric moisture and carbon dioxide, was kept at 35—40° for 24 hours with occasional

shaking.* Water (500 c.c.) was now added to dissolve the cake of the potassium derivative of 2-nitro-4 : 5-dimethoxyphenylpyruvic acid which had separated, and the purple aqueous layer, after separation, was washed with a little benzene and acidified with a slight excess of dilute hydrochloric acid. A copious sandy precipitate of the above acid was immediately formed, which when dried was sufficiently pure for use in the next stage of the synthesis. A further small amount could be isolated by exhaustively extracting the combined benzene–ether layers with 5% caustic soda solution and then acidifying the alkaline extract. The total yield was 40 g. or 60% of the theoretical, and most (16 g.) of the unchanged 6-nitro-homoveratrole was recovered by evaporation of the combined benzene–ether layers.

2-Nitro-4 : 5-dimethoxyphenylpyruvic acid is sparingly soluble in water and readily soluble in the usual organic solvents with the exception of light petroleum, and glacial acetic acid, from which it crystallises in clusters of bright yellow, microscopic needles, m. p. 193—194°, with evolution of gas at 197° (Found : C, 48·85; H, 4·0. $C_{11}H_{11}O_7N$ requires C, 49·1; H, 4·1%). It dissolves in dilute aqueous caustic soda to a deep permanganate-purple solution, the colour being discharged on long standing. Its aqueous-alcoholic solution gives a deep greenish-black colour with ferric chloride stable to acetic acid but destroyed by dilute mineral acids.

The *phenylhydrazone* was obtained by boiling a solution of the acid (0·32 g.) and phenylhydrazine (0·13 g.) in glacial acetic acid (20 c.c.) for 30 minutes. On dilution with much water the phenylhydrazone separated as a sandy precipitate which was crystallised first from benzene and then from 50% acetic acid, from which it separated in minute plates (parallelipipeds) which darken at 165° and melt at 170° with vigorous decomposition (Found : C, 57·3; H, 5·15. $C_{17}H_{17}O_6N_3$ requires C, 56·8; H, 4·8%).

2-*Nitro*-4 : 5-*dimethoxyphenylacetic Acid*.—The pyruvic acid (0·42 g.), dissolved in 2% caustic soda solution (3·5 c.c.) and cooled in ice, was oxidised by the careful addition of hydrogen peroxide (20 volume; 8 c.c. in all) until the colour had been discharged; more 2% caustic soda solution and hydrogen peroxide were then cautiously added until the liquid was permanently decolorised. The pale

* The mode of effecting the condensation described by Kermack, Perkin, and Robinson (J., 1921, **119**, 1630) which gave good results with *o*-nitro-*p*-tolyl methyl ether, *viz.*, digestion of the *o*-nitrotoluene with an alcoholic solution of sodium ethoxide and ethyl oxalate, is not to be recommended for the above, since one obtains a gummy product, very difficult to purify and not giving satisfactory results if used as such for the preparation of the indolecarboxylic acid.

yellow precipitate obtained on acidification was collected and crystallised from dilute acetic acid, from which it separated in almost colourless needles, m. p. 202—204° with slight decomposition to a red liquid (Found: C, 50·2; H, 4·5. $C_{10}H_{11}O_6N$ requires C, 49·8; H, 4·6%). It is readily soluble in ethyl acetate and glacial acetic acid, and sparingly soluble in benzene, chloroform, and cold water.

5 : 6-*Dimethoxyindole-2-carboxylic Acid* (III).—2-Nitro-4 : 5-dimethoxyphenylpyruvic acid (38 g. of crude product) was dissolved in ammonia (213 c.c., *d* 0·880, mixed with 300 c.c. of water) and reduced by the addition of a hot solution of ferrous sulphate (274 g. of hydrated crystals in 300 c.c. of water). The mixture was heated on the steam-bath for 30 minutes with frequent shaking, and finally gently boiled for the same length of time. The liquid was filtered while hot, and the precipitate of ferric oxide washed with hot water containing a little ammonia. The dark brown filtrate was acidified by the addition of a very slight excess of *N*-sulphuric or, preferably, *N*-phosphoric acid, and the precipitated indolecarboxylic acid at once filtered off and dried in a vacuum. The yield is poor, but can be increased somewhat by immediately extracting the mother-liquor with ether. Purification of the acid is best effected by crystallising it first from hot water (charcoal) and then repeatedly from benzene, from which it separates in colourless plates, m. p. 202—203° (decomp.). Well-formed, rhombohedral tablets are deposited if a hot solution of the acid (0·5 g.) in acetone (10 c.c.) and benzene (100 c.c.) is allowed to cool slowly. The acid can also be crystallised from chloroform, in which it is sparingly soluble in the cold (Found: C, 59·9; H, 5·3. $C_{11}H_{11}O_4N$ requires C, 59·7; H, 5·0%). On warming with *p*-dimethylaminobenzaldehyde and a drop of hydrochloric acid a pale purple colour is obtained which becomes redder on the addition of a trace of nitrite.

When a trace of nitric acid is added to a very dilute solution of the acid in glacial acetic acid, a yellow colour is developed, deepening to golden-yellow on warming. The acid itself dissolves in concentrated sulphuric acid to an orange solution, but addition of a trace of nitric acid merely brings about partial decoloration to pale yellow.

Attempts to obtain the ethyl ester (already described by Perkin and Rubenstein, *loc. cit.*) by the ordinary methods were unsuccessful owing to the instability of the acid in presence of mineral acids.

5 : 6-*Dimethoxyindole.*—5 : 6-Dimethoxyindole-2-carboxylic acid, contained in a small Claisen flask with a long side-arm, was heated in an oil-bath at 205—215° for ½ hour. When a quiet melt had been obtained, the flask was transferred to a fusible-metal bath, and its

contents distilled in a vacuum. The indole came over at 198°/8 mm. and solidified at once in the side-arm, which was afterwards severed from the flask and ground up with dilute potassium carbonate solution, and the solid material collected and extracted with boiling 95% alcohol, from which the indole separated, on cooling, in a state of purity, m. p. 154—155° unaltered by further crystallisations. 5 : 6-Dimethoxyindole crystallises from benzene in rods, from 95% alcohol and from light petroleum (in which it is very sparingly soluble) in colourless, glistening leaflets, and from 50% alcohol, by slow deposition, in long, coarse needles (Found : C, 67·6; H, 6·2; N*, 8·2; MeO, 34·0. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2; N, 7·9; MeO, 35·0%).

This indole quickly darkens on keeping and is very sensitive to oxidising agents in the presence of acids. Although insoluble in cold, dilute hydrochloric acid, it slowly develops a brown colour in contact with this acid, and, on warming, dissolves with almost immediate production of the brown colour. Addition of ferric chloride to an aqueous-alcoholic solution of the indole produces a permanent deep green coloration. With *p*-dimethylaminobenzaldehyde and hydrochloric acid the indole gives a rich purple colour and on addition of a trace of nitrite this changes to a deep crimson.

When equivalent quantities of the indole and of picric acid were dissolved in hot acetone or methyl alcohol, a deep red solution was obtained; this, on evaporation, yielded a deep purple, gummy picrate, which could not be obtained crystalline.

1-*Acetyl*-5 : 6-*dimethoxyindole* is formed in poor yield when 5 : 6-dimethoxyindole (0·4 g.) is boiled for 5½ hours with acetic anhydride (10 c.c.) and freshly-fused sodium acetate (1·2 g.). The cooled mixture is diluted with ether and filtered, and the filtrate evaporated in a vacuum, finally at 80°. The red, oily residue is then repeatedly extracted with boiling light petroleum (b. p. 60—80°), from which the acetyl derivative crystallises in minute, yellowish-brown, ill-defined leaflets, m. p. 150—152° (Found : C, 66·4; H, 6·2. $C_{12}H_{13}O_3N$ requires C, 65·8; H, 6·0%). A mixture of the indole and this derivative melted at 144—147°.

Neither 5 : 6-dimethoxyindole nor its 1-acetyl derivative gives the brucine reaction (compare Perkin and Rubenstein, *loc. cit.*, on ethyl 5 : 6-dimethoxyindole-2-carboxylate). In each case addition of a

* All the compounds described in this communication were analysed for nitrogen by the Pregl–Dumas method, and high results (0·3—1·5%) were consistently obtained. It seems well established that certain anisyl and veratryl derivatives during combustion are liable to give off methane, which gas is not completely oxidised when passed over hot copper oxide (compare Bradley and Robinson, J., 1926, 2361).

little nitric acid to a very dilute solution of the substance in glacial acetic acid produces a yellow tint only, changing to golden-brown on gentle warming. On standing, the colour becomes brownish-red. The indole gives no coloration, and the acetyl derivative a pale green colour, with concentrated sulphuric acid, but in each case addition of a trace of nitric acid at once produces an intense greenish-brown colour, changing quickly to brownish-red and, on standing, to pure red.

THE UNIVERSITY, MANCHESTER. [*Received, December 22nd,* 1926.]

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## LXIII.—*The Soluble Alkaline-Earth Aluminates.*

By HUBERT THOMAS STANLEY BRITTON.

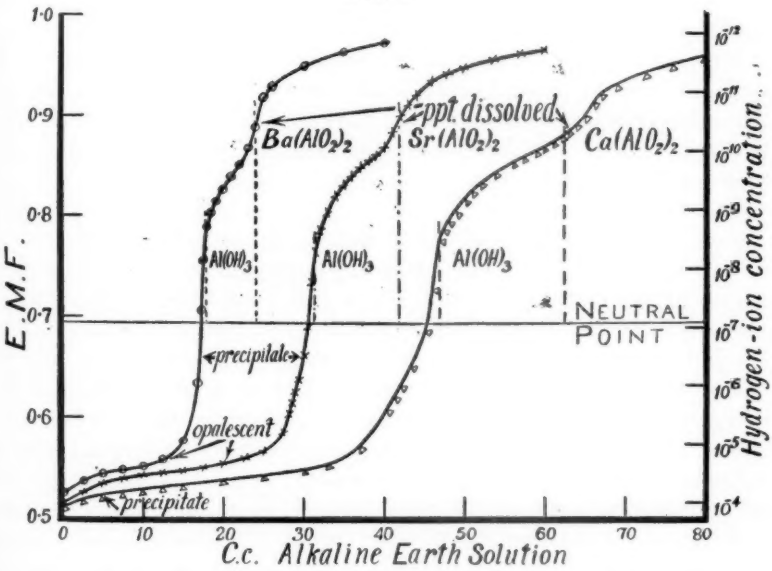
It is often stated that the aluminates of calcium, barium, and strontium are very sparingly soluble in water. Thus Marais (*Soil Science*, 1922, **13**, 368) asserts that lime removes alumina from a "soil solution" as a very sparingly soluble calcium aluminate, $Ca_3Al_2O_6$. Alumina, besides being present in soil solutions of which the hydrogen-ion concentrations are greater than that at which aluminium hydroxide begins to be precipitated, *viz.*, $10^{-4\cdot2}$ (compare Britton, J., 1925, **127**, 2121), is sometimes found in slightly alkaline soil solutions, of $p_H$ about 9 (Magistad, *Soil Sci.*, 1925, **20**, 181). Pollard and Keast (private communication) found that it passed into the soil solution at $p_H$ 7·7—8·6, as the result of treating soil with slaked lime, and, moreover, they observed that the aluminium content increased with the calcium content. It was suspected that the explanation lay in the formation of a soluble calcium aluminate. In order to test this supposition, the following titrations of dilute solutions of aluminium salts were carried out with solutions of each of the alkaline earths, the concentrations of which are given in Table I, and the changes in hydrogen-ion concentration were determined by means of the hydrogen and normal calomel electrodes, in the manner described in previous papers (J., 1924, **125**, 1572; 1925, **127**, 2110), the junction being a saturated solution of potassium chloride. The temperature was 20°.

The curves (see Fig. 1.) are similar to that obtained by using sodium hydroxide (J., 1925, **127**, 2121). The $p_H$'s at which precipitation began in the three reactions are widely different, although those sections of the three curves which correspond to the formation of aluminium hydroxide cover approximately the same variation in hydrogen-ion concentration. Thus in the lime titration, in which the sulphate was employed, precipitation began when only

TABLE I.

| Reactant. | Solution : 100 c.c. of | Precipitation began at: $p_H$. | Precipitation began at: Equivs. alkali per atom Al. | Precipitate dissolved at: $p_H$. | Precipitate dissolved at: Equivs. alkali per atom Al. |
|---|---|---|---|---|---|
| 0·0447*N*-$Ca(OH)_2$. | 0·00349*M*-$Al_2(SO_4)_3$. | 4·14 | 0·32 | 10·17 | 3·90 |
| 0·0558*N*-$Ba(OH)_2$. | 0·00333*M*-$AlCl_3$. | Opalescent. 4·76 | 2·09 | | |
| | | Coagulated. 6·50 | 2·71 | 10·43 | 4·02 |
| 0·0391*N*-$Sr(OH)_2$. | 0·00408*M*-$AlCl_3$. | Opalescent. 4·69 | 1·92 | | |
| | | Coagulated. 6·50 | 2·88 | 10·60 | 4·02 |

FIG. 1.




0·32 equiv. of alkali per atom of aluminium had been added, whereas in both the strontia and baryta titrations, in which aluminium chloride was used, the solutions remained clear until 2·09 equivs., $p_H$ 4·76, and 1·92 equivs., $p_H$ 4·69, respectively, of alkali had been added; only opalescence was then produced, coagulation of the precipitates not occurring until 2·71 and 2·88 equivs., respectively, had been added, and a considerably higher $p_H$ attained, *viz.*, 6·5. This delay in precipitation, despite the fact that the requisite precipitation $p_H$, 4·14, had been exceeded, and that nearly the total stoicheiometrical quantity of alkali had been added, is due

to the characteristic tendency of chlorides to promote the formation of colloidal solutions—the dispersed particles formed in the initial stage of the reactions being too small to affect the appearance of the solution to the unaided eye. A similar instance is that of the chloride and sulphate of zirconium (Britton, J., 1925, **127**, 2125).

The solutions became neutral when the alkaline earths had been added in amounts slightly less than those required for the formation of aluminium hydroxide owing to the retention by the precipitates of some of the acid radical present in the original salts. In each of the titrations, the precipitates redissolved completely when approximately another equivalent of alkaline earth had been added, the dissolutions being reflected in the characteristic aluminate inflexions of the titration curves extending over a $p_H$ range from 8 to 10·5. Magistad's results (*loc. cit.*) on the solubility of alumina in sodium hydroxide solutions of varying $p_H$ are important in that they show that the solubility first becomes perceptible at $p_H$ 7·55, being then 2 parts per million; at $p_H$ 8·35, the solubility is 8·4 parts, but thereafter it increases rapidly to 34·6 parts per million at $p_H$ 8·95. In a natural soil solution it was 31·0 parts per million at $p_H$ 9·01. Hence it appears probable that the formula $M^{\cdot\cdot}(AlO_2)_2$ represents the type of combination in which the alkaline earths and alumina exist in solution.

It should be mentioned that in the calcium titration a fine precipitate containing both calcium and aluminium began to separate at $p_H$ 11·7 when 90 c.c. of lime water had been added. It follows, therefore, that the disappearance of alumina from "soil solutions" cannot be attributed, as Marais states, to the formation of an insoluble calcium aluminate, for the hydrogen-ion concentration of ordinary "soil solutions" never becomes so low as $p_H$ 11·7. No precipitates were formed in the other two titrations, even although large excesses of the reactants were added. The conditions under which the solid aluminates of barium may exist have recently been investigated by Malquori (*Gazzetta*, 1926, **56**, 54).

The author acknowledges his indebtedness to the Department of Scientific and Industrial Research for a personal grant, and to Professor J. C. Philip, F.R.S., for kindly placing facilities at his disposal.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON. [*Received, December 3rd*, 1926.]

# LXIV.—*Electrometric Study of the Precipitation of Silicates.*

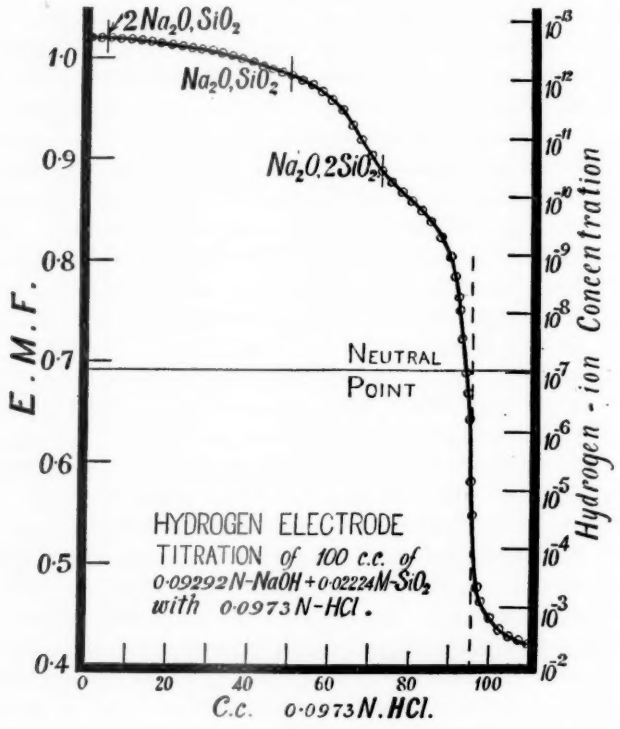
By Hubert Thomas Stanley Britton.

The work now described was undertaken in order to gain some insight into the reactivity of silicic acid towards various bases of different strengths. Its reaction with sodium hydroxide was first studied, for, although this subject has received some attention in recent years by measurements of the hydrogen-ion concentrations of solutions of silicic acid in sodium hydroxide (Bogue, *J. Amer. Chem. Soc.*, 1920, **42**, 2575; Joseph and Oakley, J., 1925, **127**, 2814; Harman, *J. Physical Chem.*, 1926, **30**, 1100; Hägg, *Z. anorg. Chem.*, 1926, **155**, 20), there still remains much uncertainty as to the actual manner in which the acid ionises, and, moreover, the results hitherto recorded do not give a complete account of the variation in hydrogen-ion concentration throughout the course of neutralisation at 18°. Joseph and Oakley concluded, from $p_H$ measurements at 33—38° of solutions of water-glass to which varying amounts of acid or alkali had been added, that the neutralisation curve obtained was "typical of the combination of a strong base with a weak dibasic acid," $K_1$ being about $10^{-10}$, and $K_2$ about $10^{-12}$, the symbols relating to the first and second dissociation constants, respectively. Hägg also states that, if silicic acid is not colloidal, $K_1$ of metasilicic acid is of the order of $10^{-9}$ and $K_2$ about $10^{-13}$. The curve given in Fig. 1 shows the change in hydrogen-ion concentration when 100 c.c. of a solution, 0·09292*N* with respect to NaOH and 0·02224*M* with respect to $SiO_2$, were titrated at 18° with 0·0973*N*-hydrochloric acid, using the hydrogen and the normal calomel electrodes in the way previously described (J., 1924, **125**, 1572; 1925, **127**, 2110). The ratios of $Na_2O$ to $SiO_2$ present in the solution at the different stages of neutralisation are indicated on the curve. Two inflexions occurred in that portion corresponding to the addition of 2 equivs. of sodium hydroxide to 1 mol. of silicic acid, and the point corresponding to half-neutralisation of metasilicic acid, *i.e.*, $Na_2O,2SiO_2$, falls at $p_H$ 10·4 just at the beginning of the second inflexion. As other workers have shown, the ionisation of silicic acid cannot be represented satisfactorily in terms of two dissociation constants; moreover, the titration curve is not typical of a dibasic acid inasmuch as when $K_1$ and $K_2$ are widely different the point corresponding to half-neutralisation should lie somewhere about the middle of the second inflexion—in Fig. 1 it should be near the point corresponding to $p_H$ 11. The curve, however, shows that silicic acid enters into some kind of combination with sodium

hydroxide, and gives some idea of the hydrogen-ion concentrations that are thereby set up. It also shows that the hydrogen-ion concentration imparted by silicic acid to a solution is much too small to have any effect on the methyl-orange end-point, and hence the reason why the alkali present in a silicate solution may be titrated by using such an indicator.

In order to study the reactions (and consequent precipitations) between silicic acid and the alkaline earths, hydrogen-electrode

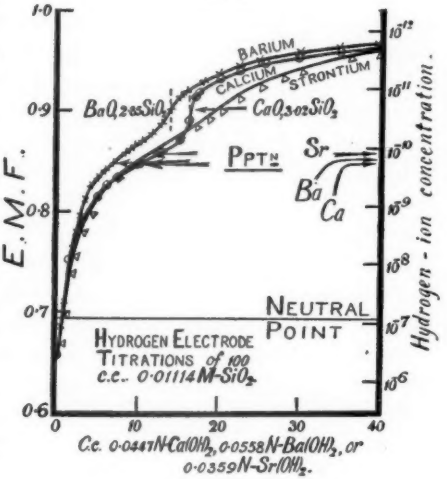
FIG. 1.




titrations were carried out at 18° of solutions of 100 c.c. of 0·01112*M*-$SiO_2$ with each of the following solutions: 0·0447*N*-calcium hydroxide, 0·0558*N*-barium hydroxide, and 0·0359*N*-strontium hydroxide. The solutions were prepared immediately before the titrations by neutralising sodium silicate solutions with hydrochloric acid, using methyl-orange, in order that they should contain the acid in a condition of maximum reactivity and that any diminution by ageing or by precipitation of the silicic acid should be avoided. These very dilute solutions were quite clear. The titration curves

given in Fig. 2 show that precipitation of the silicates did not begin until appreciable amounts of alkaline-earth solutions had been added, and when approximately the same hydrogen-ion concentrations had been attained. Thus the compositions of the solutes when on the point of precipitation were $CaO,5{\cdot}0SiO_2$; $BaO,5{\cdot}07SiO_2$; and $SrO,5{\cdot}54SiO_2$; the respective $p_H$'s being 9·74, 9·72, and 9·90. In the case of the calcium and barium titrations marked inflexions occurred between $p_H$ 10 and 11, but in the strontium titration an inflexion is scarcely perceptible. It was found that, in the calcium and barium reactions, these inflexions denoted the points when the silica and the whole of the added alkaline earths had become precipitated; hence the precipitates must have been $CaO,3{\cdot}02SiO_2,xH_2O$ and $BaO,2{\cdot}85SiO_2,xH_2O$. The hydrogen-ion concentrations of the solutions thereafter indicate that some further reaction took place between the precipitates and the additional alkaline-earth solutions. The hydrogen-ion concentrations of the solutions prior to precipitation are comparable with those produced with sodium hydroxide (*vide* Fig. 1), showing that the condition in which the silicic acid is present in both the alkali and the alkaline-earth solutions is similar. It seems reasonable to suppose that the high proportion of silica retained in the solutions must be due to some colloidal micellar formation.

FIG. 2.




The amounts of silica found in " soil solutions " of any $p_H$ are very small even when their calcium contents are comparatively high. This seems to be contrary to what might be expected from the foregoing observations. The absorption of carbon dioxide, however, is sufficient to decompose any calcium silicate solutions which may be formed.

The absorption of alkaline earths by silica gel suspended in water was marked by a slow and gradual diminution in hydrogen-ion concentration. The curves showed a " buffer action," the extent of which depended on the amount of silica employed, commencing from $p_H$ 6·5, instead of the sharp change shown in Fig. 2, where the silica was not in great excess. The buffer action of the silica gel

is comparable with that which takes place when slaked lime is added to a soil, the reaction being usually between $p_H$ 6·5 and 9.

Attention was now directed to the action of solutions of sodium silicate on typical metallic-salt solutions. The precipitates thus obtained have received comparatively little attention, and the very few formulæ which have been assigned to them show that the ratio of silica to base is always higher than that required to form the metasilicate. Some investigators have, however, mentioned that their precipitates contained free silica. The difficulties inherent in the separation of a silicate precipitate, often containing free silica, from its mother-liquor in anything approximating to the pure state (of which there is usually no criterion), are so great that it is probable that the few analyses which have been made convey no idea of the reaction which took place. It has been shown above that the acidic property of silicic acid asserts itself only in alkaline solutions, and consequently it would be expected that very little action could take place between it and those hydroxides which are precipitated from acid solutions, unless the substances formed by the interaction were extremely insoluble. The view has been advanced, however, to account for the acidity of "soil solutions," that complex alumino-silicic acids exist in the soil through the interaction of aluminium hydroxide and silica. If any such combination could take place, it is probable that it would have some effect on the hydrogen-ion concentration of the mother-liquor. It was therefore decided to investigate electrometrically the changes in hydrogen-ion concentration when solutions of sodium silicate and of metallic salts are allowed to interact. The sodium silicate employed was prepared from water-glass containing 2·16 mols. $SiO_2$ to 1 mol. $Na_2O$, and was 0·1020*N* with respect to sodium hydroxide. The impurities therein, including carbon dioxide, were so small as to have no measurable effect on the *E.M.F.* measurements. The solutions used are given in Table I, together with the $p_H$ at which precipitation began, the amount of reactant which had to be added, and the $p_H$ at which the respective hydroxides are precipitated, these values having been taken from the author's papers (J., 1925, **127**, 2110, 2120). 100 C.c. of salt solution were used for each titration.

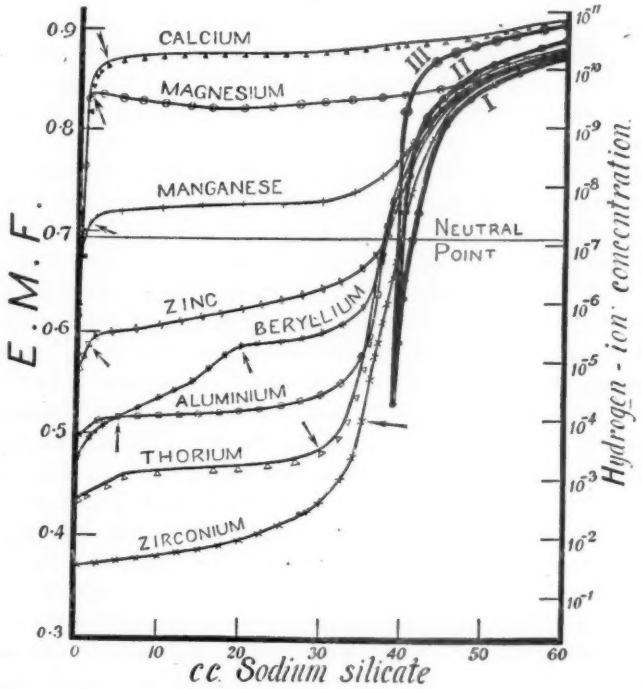
The titration curves are plotted in Fig. 3, in which the beginning of precipitation is marked by arrows. The amount of sodium silicate required in each reaction such that the alkali was in a quantity equivalent to the acid radical in 100 c.c. of salt solution was 39 c.c. The curves lying beyond 39 c.c. illustrate the effect of increasing amounts of sodium silicate on the hydrogen-ion concentration of the mother-liquor. The equation

$$Na_2O,2{\cdot}16SiO_2 + RCl_2 \longrightarrow 2NaCl + RO,xSiO_2 \downarrow + (2{\cdot}16 - x)SiO_2$$

TABLE I.

| Solution titrated. | Precipitation began at $p_H$. | Precipitation began at c.c. of sodium silicate. | Hydroxide precipitation at $p_H$. |
|---|---|---|---|
| 0·01*M*-$ZrCl_4$. | 3·98 | 35·0 | 1·86 |
| 0·01*M*-$ThCl_4$. | 3·50 | 30·0 | 3·50 |
| 0·0067*M*-$Al_2(SO_4)_3$. | 4·04 | 5·0 | 4·14 |
| 0·02*M*-$BeSO_4$. | 5·31 | 20·0 | 5·69 |
| 0·02*M*-$ZnSO_4$. | 5·25 | 1·0 | 5·20 |
| 0·02*M*-$MnCl_2$. | 7·35 | 1·0 | 8·41 |
| 0·02*M*-$MgSO_4$. | 9·50 | 1·0 | 10·49 |
| 0·02*M*-$CaCl_2$. | 10·07 | 3·0 | — |

FIG. 3.




shows that after the silicate $RO,xSiO_2$ had been precipitated by the 39 c.c., the mother-liquor comprised a sodium salt (chloride or sulphate), which through its very small concentration would have no measurable effect on the *P.D.*, and a certain amount of silicic acid which had escaped precipitation and would exert a buffering effect on the excess of sodium silicate. Some measure of the amounts of the silica which had remained in solution, and therefore of the amounts which had been precipitated with the metallic hydroxides, was obtained by following the changes in hydrogen-ion concentration

when sodium silicate, of the same concentration as that used for the precipitations, was added to solutions having the volume attained when the precipitations had become complete, *viz.*, 139 c.c., and containing the same concentration of neutral sodium salt as the original mother-liquors but different amounts of silica. Thus Curve I (Fig. 3) represents the course taken when sodium silicate was added to 139 c.c. of solution containing 39 c.c. of sodium silicate exactly neutralised (to methyl-orange) with hydrochloric acid; it would therefore have been the curve obtained if the hydroxides alone had been precipitated and all the silica had remained in solution. Curve II shows the variation in hydrogen-ion concentration which would have been produced if the metasilicates of the metals had been precipitated, and the remainder of the silica had been left in solution; whereas Curve III corresponds to the change which would have occurred if all the silica present in the 39 c.c. had been precipitated. Except for the calcium curve, those sections of the curves corresponding to an excess of sodium silicate lie between Curves I and II. Hence the amounts of silica carried down with the various precipitates were somewhat smaller than that necessary for the formation of normal metasilicates. Table I shows that the $p_H$'s at which the silicate precipitates of thorium, aluminium, and zinc separated were also those at which the respective hydroxides begin to be precipitated. In the case of the zirconium titration, the silicate precipitate did not appear until $p_H$ 3·98 was reached, as compared with $p_H$ 1·86 for the hydroxide when precipitated from chloride solution. The curve in the acid zone shows that the change in hydrogen-ion concentration was similar to that which occurred in the precipitations of the hydroxide, basic borate, and basic carbonate (J., 1926, 125). Precipitation was delayed until 3·59 equivs. of alkali had been added, whereas in the hydroxide precipitation opalescence appeared with 1·5 equivs. (Britton, J., 1925, **127**, 2133). Delayed precipitation was also noted with the basic borate and carbonate—3·4 equivs. of reactant being required in each case, and the $p_H$'s being 4·07 and 3·95, respectively. It is remarkable that the silica in the reagent should have impeded the precipitation until an almost identical $p_H$, 3·98, had been attained. The other precipitate formed whilst the mother-liquor was still acidic was that of beryllium; this began to form at $p_H$ 5·31, which is slightly lower than the hydroxide $p_H$, 5·69. As in previous work with beryllium, the precipitate did not begin to form until 1·01 equivs. of alkali, as sodium silicate, had been added. The difference in the two $p_H$'s may be due the fact that the silicic acid sol formed in the course of the reaction became very unstable on approaching the neutral point. The $p_H$'s at which the magnesium and manganese precipitates began to form are con-

siderably less than those of the respective hydroxides. The cause probably lies in the insolubility of silicic acid, which cannot therefore retain a base in solution until the hydroxide $p_H$ is reached. This is not the case with those precipitates which are formed in acid solutions, for then the acid liberated by the hydrolysis of the salts is sufficient to maintain solution until the corresponding hydroxide $p_H$ is attained, or nearly so. The interaction of sodium silicate and a solution of calcium chloride produced a curve which shows that when the stoicheiometrical amount of alkali, as silicate, had been added, the alkalinity of the mother-liquor was greater than that which would have been set up if all the silica in the sodium silicate had been removed from solution by the calcium precipitate and an excess of alkali had been added instead of sodium silicate. In the other reactions investigated, it is probable that, owing to the great weakness of silicic acid, very little or no combination took place between it and the various hydroxides, the silica in the precipitates having been the result of simultaneous precipitations. It is nevertheless surprising that all the silica attached to those portions of the reagents which were responsible for the precipitations was not itself completely precipitated with the hydroxides. It is, of course, possible that the excess of sodium silicate which was subsequently added peptised some of the silica which had originally been precipitated. The formation of silicate precipitates is probably the result of the mutual coagulation of oppositely charged colloids through the removal by neutralisation of the substances which tended to stabilise or to peptise them, as found by Thomas and Johnson (*J. Amer. Chem. Soc.*, 1923, **45**, 2532) in the case of the mutual coagulation of a ferric hydrosol, peptised by ferric chloride, and a silica sol, peptised by sodium silicate.

The precipitation of calcium silicate is, however, of quite a different nature in that calcium hydroxide is fairly soluble in water and is, moreover, sufficiently strong a base to react with silicic acid. The alkalinity of the solution was caused by the considerable hydrolysis of the calcium silicate, and the exceptionally high $p_H$ of the solution after 39 c.c. of sodium silicate had been added was apparently due to the withdrawal by the precipitate of more silica from the reagent, the precipitate thus containing more than 2 mols. of $SiO_2$ to 1 mol. of CaO.

*Discussion.*

The foregoing observations have an important bearing on the vexed question of the cause of soil acidity. In contrast with the large amount of work done to discover the cause of acidity in soils, very little has been done to ascertain what are the hydrogen-ion concentration relationships involved when any two of the con-

stituents of the soil react. Swanson (*J. Agric. Res.*, 1923, **26**, 83) has shown that the acidity arises chiefly from the mineral constituents of the soil, the part played by the organic matter being, in general, negligible. The modern view is that the varying acidity of soils is due to the presence of complex aluminosilicic acids in different stages of neutralisation (*Ann. Reports*, 1925, **22**, 203). This idea appears to have been based on some work of Bradfield (*Missouri Agr. Exp. Sta. Research Bull.*, 1923, No. 60), who concluded from a comparison of the properties of soil colloids, separated from clay, with those of a mixture of hydrated silica, alumina, and ferric oxide, that the colloidal material consisted either of a definite compound or of a mixture of compounds in which the oxides were chemically bound as aluminosilicates. He considered that the type of titration curve obtained with the hydrogen electrode when a solution of calcium hydroxide was titrated with a clay suspension was that of a weak acid, and he was therefore led to believe that the colloidal material in the soil was itself the acid (*J. Amer. Chem. Soc.*, 1923, **45**, 2669). Saint (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 134) has suggested that if a soil be represented as a partly neutralised acid, the amounts of different bases which any particular soil can absorb should be in equivalent proportions, and has advanced evidence to support the view in the case of the alkalis and the alkaline earths when considered separately, the difference between the two sets of figures being attributed to the formation of insoluble alkaline-earth salts. This, however, would be expected from a consideration of the very similar reactions which the alkaline earths and the alkalis enter into with hydrated silica (compare Figs. 1 and 2).

The reaction involving the formation of the aluminium silicate precipitate affords no evidence of the existence of a complex aluminosilicic acid (Fig. 3). It is true that if the changes in hydrogen-ion concentration are followed when such a precipitate is subjected to treatment with solutions of alkalis or alkaline earths, the precipitate exerts a pronounced buffer action, which *primâ facie* might be regarded as indicating that the precipitate was an acid. This buffer action is, however, the result of a superposition of several reactions, *viz.*, (*a*) the reaction between the aluminium hydroxide and the base to form a soluble aluminate, buffering between $p_H$ 8 and 10 (*vide* Britton, this vol., p. 424), (*b*) the reaction between the base and the hydrated silica, giving rise to a gradual rise in $p_H$ from 6 upwards, and (*c*) an equilibrium between the silicic acid and any soluble aluminate, *e.g.*, $Ca(AlO_2)_2$, which may have been initially formed, to give calcium silicate, $CaO,xSiO_2,yH_2O$, and hydrated alumina, producing a hydrogen-ion concentration from $p_H$ 6 upwards.

The amount of soluble aluminate actually formed is doubtless a function of the amount of water present. Similarly, if the inorganic colloids of the soil be considered as mixtures chiefly of hydrated alumina and silica, then the effect on the hydrogen-ion concentration of adding slaked lime to the soil would be determined by the reactivity of the two constituents with the lime. The titration curves of Hissink and van der Spek (*Trans. 2nd Comm. Internat. Soc. Soil Sci.*, Gröningen, 1926, 72) with the hydrogen electrode of soil suspensions all show buffer action between $p_H$ 6 and 8.

The curves given in Fig. 3 also account for the presence of various metals in soil solutions of different $p_H$ reactions. Magistad (*Soil Sci.*, 1925, **20**, 181) has found that aluminium appears in soil solutions only when the $p_H$ is lower than 4·0—4·5 or higher than 8. The limit on the acid side is seen to correspond with the $p_H$ range at which aluminium hydroxide or silicate is precipitated (Fig. 3), and, as pointed out previously (this vol., p. 424), its reappearance in alkaline solutions is due to the acidic behaviour of the aluminium hydroxide exerting itself. Many chemists have also found alumina in the neutral-salt extracts of sour soils; thus, by the use of potassium chloride or nitrate, sodium chloride, etc., Veitch (*J. Amer. Chem. Soc.*, 1904, **26**, 637) concluded that the addition of sodium chloride to a soil did not liberate hydrochloric acid as such but aluminium chloride, and therefore the acidity was only apparent. Knight's (*Ind. Eng. Chem.*, 1920, **12**, 343) analysis of a soil extract with potassium nitrate shows that 90% of the titratable acid was in combination with alumina. Rice (*J. Physical Chem.*, 1916, **20**, 214) found aluminium in potassium nitrate extracts of which the $p_H$'s ranged from 3·5 to 4·5. Niklas and Hock (*Z. angew. Chem.*, 1925, **38**, 195) have titrated potassium chloride extracts of soils with sodium hydroxide, using the hydrogen electrode. The first branch of their curve, corresponding to the decomposition of the aluminium salt, lies at about $p_H$ 4 (compare Fig. 3), and the remaining section shows a buffer action up to just above $p_H$ 8. The acidity of the more acidic soils is due to the normal hydrolysis of the aluminium salts formed in the soil.

The $p_H$ of soil solutions from sour soils after treatment with neutral salts often becomes still lower; thus Crowther (*J. Agric. Sci.*, 1925, **15**, 212) found that soils of $p_H$ 4·78 on treatment with neutral salts gave about $p_H$ 4. Soils of $p_H > 6$ appear to be unaffected by neutral salts, and their titratable or " mineral " acidity becomes negligible (compare Christensen and Jensen, *Trans. 2nd Comm. Internat. Soc. Soil. Sci.*, Gröningen, 1926, 111). The mineral acidity given by acid soils appears to depend on the extent to which neutral salts, when allowed to react upon soils, are able to cause an increase

in hydrogen-ion concentration above that requisite for the precipitation of aluminium hydroxide, and thereby to enable alumina to pass into solution as a salt. The fact that the hydrogen-ion concentrations of such soil solutions are nearly the same as that at which aluminium hydroxide is normally precipitated suggests that the soil must contain some aluminium hydroxide in a partly neutralised state (*vide* Britton, J., 1925, **127**, 2120). This would, on hydrolysis through contact with water, give a $p_H$ near that at which aluminium hydroxide becomes precipitable. When a neutral-salt solution is added to such a soil, it is probable that the salt splits up, the basic part combining with the preponderance of silicic acid and being retained by the soil, and the acidic part combining with the partly neutralised aluminium hydroxide to enable some aluminium salt to pass into solution. Thus sodium chloride might be considered to split up into sodium oxide and hydrochloric acid, the sodium oxide attaching itself to the large excess of colloidal silica and thus becoming insoluble, whereas the hydrochloric acid, in reacting with the aluminium hydroxide, causes some aluminium chloride to pass into solution and thereby increases the hydrogen-ion concentration and the titratable acidity. It is significant that this "exchange" acidity disappears almost completely from soils of $p_H$ 6 and above. It is at this point that aluminium hydroxide acquires its optimum insolubility, due to the withdrawal of the small amount of acid radical which it retained on being precipitated. Above this point, it behaves as an acid and consequently is without effect on neutral salts.

Manganese has been found in solutions from certain acid soils. Pollard (private communication) has found it in solutions of $p_H$ up to 6 from certain sour soils. Rice (*loc. cit.*) found it in potassium nitrate extracts up to $p_H$ 5 of acid soils. Fig. 3 shows that the precipitation of manganese silicate does not begin until just above $p_H$ 7. The $p_H$ of manganous salt solutions is of the order 5—6, but it must be remembered that, when a manganous salt solution is treated with alkali in a quantity insufficient to start precipitation, the solution rapidly decomposes through oxidation and brown oxide separates. Hence it is unlikely that manganese would be found in a soil solution of $p_H > 6$.

Although ferric oxide is often a constituent of soils, very little can pass into the soil solution, except in colloidal form, because it is precipitated from strongly acid solutions (Britton, J., 1925, **127**, 2155). It can, however, sometimes be detected in the neutral-salt extracts of sour soils by testing with an alcoholic solution of potassium thiocyanate (Comber's test). Pollard (private communication) found that by adding hydrochloric acid to soils, the

iron content of the aqueous extracts only became perceptible when the solutions had become more acid than $p_H$ 1·5.

The phenomenon of base exchange as exemplified by soils has been attributed to the existence of zeolitic combinations in the inorganic colloidal matter, in spite of the fact that zeolites themselves do not occur in soils. The compositions of most of the zeolites may be expressed by the general formula

$$RO,Al_2O_3,xSiO_2,yH_2O,$$

where R may represent one atom of a bivalent metal or two of a univalent metal, and $x =$ or $>2$. For Gans's synthetic permutites $x$ varied from 3 to 4. They were prepared by the action of alkali-metal aluminate solutions on silicic acid, and not by the action of alkali-metal silicate on aluminium hydroxide. It has been shown (Britton, *Analyst*, 1921, **46**, 363; J., 1925, **127**, 2120; this vol., p. 424) that the amounts of alkali or alkaline earth which dissolve aluminium hydroxide to form the soluble aluminate are approximately the same as those indicated by the formula $R^IAlO_2$, *viz.*, either 1 mol. $R^I_2O$ or 1 mol. $R^{II}O$ to 1 mol. $Al_2O_3$. This happens to be the ratio found in zeolites. Calcium aluminate solution on reacting with silicic acid, as either sol or gel, decomposes between $p_H$ 7 and 9 to give precipitates of calcium silicate (indefinite) and aluminium hydroxide, the aggregate composition of the precipitates being $CaO,Al_2O_3,xSiO_2,yH_2O$. Hence, it may be that the "base exchange" exhibited both by zeolites and by soils is due to the similarity of their active constituents.

*Summary.*

(1) The reactions between silicic acid and sodium hydroxide or the alkaline earths in solution, and those between solutions of typical metallic salts and sodium silicate, have been investigated by means of the hydrogen electrode.

(2) Although the mode of ionisation of silicic acid cannot be expressed in terms of dissociation constants, its reactions with the stronger bases have a pronounced effect on the hydrogen-ion concentrations of the solutions.

(3) The precipitates obtained by the interaction of a solution of sodium silicate, $Na_2O,2{\cdot}16SiO_2$, and metallic-salt solutions, except that of calcium chloride, contained less silica than that required to form the metasilicates.

(4) The hydrogen-ion concentrations at which these silicate precipitates began to form in solutions of $p_H$ less than 7 were approximately those at which their corresponding hydroxides separate. The silicate precipitates obtained from alkaline solutions appeared

when the hydrogen-ion concentrations had not been reduced to the extent required by their respective hydroxides.

(5) The results have been discussed in relation to the question of soil acidity.

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## LXV.—*The Inhibitory Effect of Substituents in Chemical Reactions. Part I. The Reactivity of the Amino-group in Substituted Arylamines.*

By GEORGE MALCOLM DYSON, HERBERT JOHN GEORGE, and ROBERT FERGUS HUNTER.

IN a study of the effect of substituents of different polar and steric character in certain organic chemical reactions, the first problem which it appeared desirable to investigate was the effect on the reactivity of the amino-group in substituted anilines; for this purpose, the reaction by which we have synthesised numerous thiocarbimides and thiocarbamides (J., 1924, **125**, 1702; *J. Soc. Chem. Ind.*, 1926, **45**, 83T; *Rec. trav. chim.*, 1926, **45**, 421) appeared well suited.

A primary amine can react with thiocarbonyl chloride to give two substances. The primary product is a thiocarbamyl chloride (equation A). This, in the presence of water, normally loses hydrogen chloride, yielding the corresponding thiocarbimide (equation B). When, however, inhibitory groups are present, the thiocarbamyl chloride loses hydrogen chloride with considerable reluctance and reacts with a second molecule of the amine to give the *s*-diarylthiocarbamide (equation C).

$$NH_2R + CSCl_2 = NHR{\cdot}CSCl + HCl \quad . \quad . \quad (A)$$

$$NHR{\cdot}CSCl \xrightarrow{H_2O} RNCS + HCl \quad . \quad . \quad . \quad (B)$$

$$NHR{\cdot}CSCl + NH_2R = CS(NHR)_2 + HCl \quad . \quad . \quad . \quad (C)$$

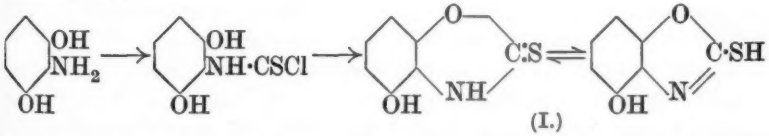
The ability of the thiocarbamyl chloride to eliminate hydrogen chloride is therefore a measure of the influence of the substituent on the reactivity of the original amine. When several inhibitory groups are present, as, for instance, in *s*-tribromoaniline and 2 : 4 : 6-trinitroaniline, inhibition of the reaction (A) may take place.

The various arylamines were treated with excess of thiocarbonyl chloride in the presence of water under standard conditions. When the amine was reactive, as in the nuclear methyl-substitution derivatives of aniline, the reaction was usually complete in 10 minutes and the thiocarbimide was isolated in 80—90% yield. When slight inhibition was present, as in the monochloroanilines (Dyson, George, and Hunter, J., 1926, 3041), thiocarbimide formation took place to the extent of about 60—70%, but the reaction was much slower, requiring about 30 minutes. When the reactivity of the amino-group was considerably depressed, as in anthranilic acid, the reaction with thiocarbonyl chloride was exceedingly slow and the only isolable product was the *s*-diarylthiocarbamide. With substances such as 2 : 6-dichloroaniline, no reaction whatever took place under these conditions; such amines were also recovered unchanged after being heated at 180° with thiocarbonyl chloride under pressure.

The experiments described in this paper are not a crucial test of the reactivity of arylamines, but are merely preliminary experiments carried out in connexion with a comprehensive study of the inhibition of organic reactions; the quantitative results will be published later.

The experiments of Dyson and Hunter (*J. Soc. Chem. Ind.*, **1926**, **45**, 83T) have shown that no possible combination of nuclear methyl groups appreciably affects the reactivity of the amino-group towards thiocarbonyl chloride, the three toluidines, *o*-4-, *m*-4-, and *p*-xylidines, *ψ*-cumidine, mesidine, and aminopentamethylbenzene all giving nearly quantitative yields of the corresponding thiocarbimides. We have since found that *o*-3- and *m*-2-xylidines also behave normally in this respect.

The effect of a hydroxyl group in the ortho-position to the amino-group cannot be directly determined, since it reacts with the chlorine atom of the intermediate thiocarbamyl chloride with the formation of a 1-thiobenzoxazole. Its effect on the amino-group appears, however, to be slight, since 2 : 6-dihydroxyaniline reacts readily with thiocarbonyl chloride, giving 3-hydroxy-1-thiobenzoxazole (I).




(I.)

The methoxy- and the ethoxy-group also have only a slight inhibitory effect on the amino-group, since the three anisidines, 3 : 4-, 2 : 5-, and 2 : 6-dimethoxyanilines, and the three phenetidines

all react normally with thiocarbonyl chloride, giving the corresponding thiocarbimides.

The effect of the cyano-group appears to lie between those of the alkyloxy-groups and the halogens, since *m*- and *p*-cyanoanilines and 2 : 5-dicyanoaniline react fairly readily, giving the corresponding cyano-substitution derivatives of phenylthiocarbimide.

Chlorine atoms considerably depress the reactivity of the amino-group in the chloroanilines; two *o*-chlorine atoms are necessary, however, for complete inhibition (Dyson, George, and Hunter, *loc. cit.*). Since the reaction becomes progressively easier with *o*-chloroaniline, *o*-bromoaniline, and *o*-iodoaniline, the effect of a halogen substituent is clearly due to a combination of both steric and polar effects. Indeed, the reaction between thiocarbonyl chloride and *o*-iodoaniline is very vigorous and is accompanied by a considerable evolution of heat (almost sufficient in our experiments to cause the supernatant water to boil). The hindering effect of an *o*-halogen atom does not appear to be affected by replacement of the second *o*-hydrogen atom by a methyl group, since 3 : 5-dibromo-*o*-toluidine reacted normally with thiocarbonyl chloride, giving 3 : 5-*dibromo*-*o*-*tolylthiocarbimide*, under conditions in which the isomeric 2 : 4 : 6-tribromo-*m*- and 3 : 5-dibromo-*p*-toluidines were recovered unchanged.

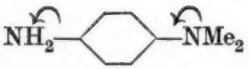
The effect of the nitro-group is very similar to that of the chlorine atom : *o*-, *m*-, and *p*-nitrophenylthiocarbimides were obtained from the corresponding nitroanilines with some difficulty, and complete inhibition was observed in the cases of 2 : 4- and 2 : 6-dinitroanilines and 2 : 4 : 6-trinitroaniline. On the other hand, 3 : 5-dinitroaniline reacted with thiocarbonyl chloride with difficulty, giving s-*bis*-3 : 5-*dinitrophenylthiocarbamide*. So far as we are aware, this is the first recorded instance of a 2 : 4-disubstituted benzene derivative being less reactive than the 3 : 5-isomeride. Further confirmation of the marked inhibitory effect of *o*-halogeno- and of nitro-substituents was obtained by an examination of 3-nitro-*o*-toluidine and 2-nitro-*p*-phenetidine, which reacted sluggishly with thiocarbonyl chloride, giving the corresponding thiocarbimides, and of 2 : 6-dichloro-, 2 : 6-dibromo-, and 2 : 6-di-iodo-*p*-nitroanilines, 4 : 6-dibromo-*o*-nitroaniline, and 2 : 4 : 6-tribromo-*m*-nitroaniline, with all of which complete inhibition was observed.

These results throw grave doubt on the theory of steric hindrance which attributes inhibition to the decrease of free space caused by the substituent (Henry, *Ber.*, 1877, **10**, 2041; Wegscheider, *Monatsh.*, 1895, **16**, 137; Angeli, *Atti R. Accad. Lincei*, 1896, **1**, 84), particularly since the molecular volumes of the methoxy- (37·1) and the methyl (25·5) group (Le Bas, "The Molecular Volumes of

Liquid Chemical Compounds") are considerably greater than the atomic volume (22·1) of chlorine.

Finally the effects of acidic and basic groups were studied. The sulpho- and the carboxyl group both exert strong inhibitory actions, the former being the more powerful, since sulphanilic acid could not be induced to react with thiocarbonyl chloride, whereas anthranilic acid was very slowly converted into s-*di*-o-*carboxyphenylthiocarbamide*.

The experiments of Billeter and Steiner (*Ber.*, 1887, **20**, 228) indicate that there is no appreciable steric hindrance due to the amino-groups in the phenylenediamines. Acylation of one amino-group, however, depresses the reactivity of the other, since s-*di*-p-*acetamidophenylthiocarbamide* is the only product isolable from *p*-aminoacetanilide and thiocarbonyl chloride and is only formed very slowly in the presence of water at 100°. Alkylation has little effect on the amino-group, since *as*-dimethyl-*p*-phenylenediamine readily passes into p-*dimethylaminophenylthiocarbimide* under the usual conditions. This would appear to be explicable on the "electron sink" properties of the carbonyl group (Allan, Oxford, Robinson, and Smith, J., 1926, 401), in which case the effect would be expected to be still more strikingly manifested in *p*-aminoacetophenone as shown in the formulæ (II) and (III).

(II.)  (III.)

*p*-Aminoacetophenone, however, reacts with thiocarbonyl chloride under the usual conditions with the greatest ease, giving a 70% yield of the corresponding thiocarbimide.

A point of interest in connexion with the organoleptic properties of thiocarbimides is that the *o*-substituted derivatives usually have an unpleasant pungent odour, whereas the *p*-substituted derivatives are invariably associated with the pleasant odour of aniseed.

## Experimental.

### *Rapid Thiocarbimide Formation.*

The thiocarbimides described below were usually obtained as follows: Thiocarbonyl chloride (1·3 mols.) was completely suspended in water (10 vols.) at 15° by vigorous stirring during the addition of a solution of the arylamine (1 mol.) in chloroform (5 vols.). After 15 minutes' stirring, the chloroform layer was removed and dried with calcium chloride, and the solvent and the excess of thiocarbonyl chloride were distilled off on a steam-bath. The thiocarbimide was obtained either by fractionating (under reduced or atmospheric

pressure according to the nature of the compound) or by steam-distilling the residue.

The arylthiocarbamides, $NHAr{\cdot}CS{\cdot}NH_2$, were prepared from the respective thiocarbimides and warm alcoholic ammonia, and the *s*-diarylthiocarbamides, $CS(NHAr)_2$, by condensing the thiocarbimides (1 mol.) with the corresponding arylamines (1 mol.) in alcohol.

m-*Xylyl*-2-*thiocarbimide* was obtained from *m*-2-xylidine by fractionation of the residue after removal of the solvent and the excess of thiocarbonyl chloride, and distilled as a colourless oil, b. p. 247°/760 mm. (Found: S, 19·8. $C_9H_9NS$ requires S, 19·6%). m-*Xylyl*-2-*thiocarbamide* crystallised from alcohol in minute, square prisms, m. p. 190° (Found: S, 19·0. $C_9H_{12}N_2S$ requires S, 18·8%). s-*Di*-m-*xylyl*-2-*thiocarbamide* crystallised in glistening, flat plates, m. p. 208° (Found: S, 11·4. $C_{17}H_{20}N_2S$ requires S, 11·3%).

o-*Xylyl*-3-*thiocarbimide* was obtained from *o*-3-xylidine (0·75 g.) and isolated by microdistillation as a colourless oil of pungent odour, b. p. 262—263°/760 mm. (yield, 0·8 g.). o-*Xylyl*-3-*thiocarbamide* crystallised from alcohol in brilliant, white needles, m. p. 182° (Found: S, 18·5%).

o-*Anisylthiocarbimide* was obtained from *o*-anisidine, and distilled as a pale yellow oil of unpleasant odour, b. p. 266—267°/760 mm. (Found: S, 19·2. $C_8H_7ONS$ requires S, 19·4%). o-*Anisylthiocarbamide* crystallised in white needles, m. p. 148—149° (Found: S, 17·2. $C_8H_{10}ON_2S$ requires S, 17·6%). s-*Di*-o-*anisylthiocarbamide* formed glistening prisms, m. p. 134° (Found: S, 11·0. $C_{15}H_{16}O_2N_2S$ requires S, 11·1%).

m-*Anisylthiocarbimide* was prepared from *m*-anisidine and distilled as a colourless oil of pungent odour, b. p. 267°/760 mm. (Found: S, 19·3%). m-*Anisylthiocarbamide* crystallised in glistening prisms, m. p. 160° (Found: S, 17·0%). s-*Di*-m-*anisylthiocarbamide* separated from alcohol in clear, crystalline plates, m. p. 126° (Found: S, 13·2%).

*p*-Anisylthiocarbimide is a pale yellow oil having a pleasant odour of aniseed, b. p. 280—281°/760 mm. *p*-Anisylthiocarbamide forms small prisms, m. p. 211°, and *s*-di-*p*-anisylthiocarbamide, small, glistening plates, m. p. 187°.

2 : 5-Dimethoxyaniline was most conveniently prepared as follows: A solution of quinol (20 g.) in 35% potassium hydroxide was treated with 50 c.c. of methyl sulphate, giving 24 g. of *p*-dimethoxybenzene, m. p. 56°; this was converted into 2 : 5-dimethoxynitrobenzene by nitration with nitric acid (*d* 1·2) in glacial acetic acid, and the nitro-derivative reduced with tin and hydrochloric acid. The dimethoxyaniline, isolated by means of ether, separated from dilute alcohol in small crystals, m. p. 84° (Magatti, *Ber.*, 1881,

14, 71; Baessler, *Ber.*, 1884, **17**, 2119). The compound rapidly turned red on exposure to the atmosphere.

2 : 5-*Dimethoxyphenylthiocarbimide*.—The dark-coloured mixture obtained on addition of the dimethoxyaniline (8 g.) to thiocarbonyl chloride in water was steam-distilled, and the distillate extracted with chloroform, yielding the thiocarbimide in large crystals, m. p. 32° (to an oil of pungent odour). 2 : 5-*Dimethoxyphenylthiocarbamide* forms small crystals, m. p. 161°, from alcohol (Found : S, 15·3. $C_9H_{12}O_2N_2S$ requires S, 15·1%). s-*Bis*-2 : 5-*dimethoxyphenylthiocarbamide* forms small crystals, m. p. 127° (Found : S, 9·3. $C_{17}H_{20}O_4N_2S$ requires S, 9·2%).

3 : 4-*Dimethoxyphenylthiocarbimide* was obtained from 3 : 4-dimethoxyaniline (prepared from 4-nitroveratrole) as an oil of pungent odour similar to that of phenylthiocarbimide; it could not be crystallised (Found : S, 17·0. $C_9H_9O_2NS$ requires S, 16·4%). 3 : 4-*Dimethoxyphenylthiocarbamide* separated from alcohol as a microcrystalline powder, m. p. 234° (Found : S, 15·0%). s-*Bis*-3 : 4-*dimethoxyphenylthiocarbamide* formed white prisms, m. p. 140°.

o-*Ethoxyphenylthiocarbimide* was obtained from *o*-phenetidine, as a pale yellow oil, b. p. 273—275°/760 mm. (Found : S, 18·0. $C_9H_9ONS$ requires S, 17·9%). o-*Ethoxyphenylthiocarbamide* crystallised from dilute alcohol in small crystals, m. p. 126° (Found : S, 16·5. $C_9H_{12}ON_2S$ requires S, 16·3%). s-*Di*-o-*ethoxyphenylthiocarbamide*, after three recrystallisations from dilute alcohol, formed large prisms, m. p. 125° (Found : S, 10·0. $C_{17}H_{20}O_2N_2S$ requires S, 10·2%).

m-*Ethoxyphenylthiocarbimide* was obtained from *m*-phenetidine as a clear, colourless oil of pungent odour, b. p. 278°/758 mm. (Found : S, 17·8%). m-*Ethoxyphenylthiocarbamide* formed short, white prisms, m. p. 167° (Found : S, 16·6%). s-*Di*-m-*ethoxyphenylthiocarbamide* separated from alcohol in aggregates of coarse needles, m. p. 115° (Found : S, 10·0%).

*p*-Ethoxyphenylthiocarbimide forms large, glistening plates having the odour of aniseed, m. p. 76°. *p*-Ethoxyphenylthiocarbamide forms small crystals, m. p. 176°, and *s*-di-*p*-ethoxyphenylthiocarbamide, plates, m. p. 171°.

o-*Carbethoxyphenylthiocarbimide*.—The rate of addition of ethyl anthranilate solution in chloroform to the thiocarbonyl chloride suspension was adjusted so that the temperature did not rise above 30°. The thiocarbimide distilled under reduced pressure as a pale, thick oil of nauseating odour, b. p. 150—151°/1 mm. (Found : S, 15·0. Calc. for $C_{10}H_9O_2NS$ : S, 15·4%). *o*-Carbethoxyphenylthiocarbamide separated from 50% alcohol in needles, m. p. 300—305° (Found : S, 14·2. Calc. for $C_{10}H_{12}O_2N_2S$ : S, 14·3%).

*s*-Di-*o*-carbethoxyphenylthiocarbamide crystallised slowly from

its solutions in colourless prisms which decomposed without melting (Found: S, 8·0. Calc. for $C_{19}H_{20}O_4N_2S$: S, 8·6%).

m-*Carbethoxyphenylthiocarbimide* distilled as a pale yellow oil, b. p. 152°/10 mm. (Found: S, 15·2%). m-*Carbethoxyphenylthiocarbamide* formed long, glistening prisms, m. p. 294—295° (Found: S, 14·2%). s-*Di*-m-*carbethoxyphenylthiocarbamide* separated from alcohol in white prisms which decomposed without melting (Found: S, 8·0%). This compound was sometimes difficult to crystallise.

p-*Carbethoxyphenylthiocarbimide* crystallised from dilute alcohol in glistening plates having an odour of aniseed, m. p. 58° (Found: S, 15·3%). p-*Carbethoxyphenylthiocarbamide* formed glistening needles, m. p. 159° (Found: S, 14·0%). s-*Di*-p-*carbethoxyphenylthiocarbamide* crystallised in small prisms, m. p. 165° (Found: S, 9·0%).

p-*Dimethylaminophenylthiocarbimide* was prepared from *as*-dimethyl-*p*-phenylenediamine and thiocarbonyl chloride in the usual way; after removal of the chloroform on a steam-bath, the residue was steam-distilled for 8—10 hours, the thiocarbimide slowly passing over as an oil which solidified in pale yellow prisms, m. p. 67° (Found: S, 18·2. $C_9H_{10}N_2S$ requires S, 17·9%). p-*Dimethylaminophenylthiocarbamide* formed pale yellow prisms, m. p. 190° (Found: S, 16·0. $C_9H_{13}N_3S$ requires S, 16·4%).

p-*Acetylphenylthiocarbimide* was prepared from *p*-aminoacetophenone in the same way as the dimethylaminophenyl compound, and distilled slowly in steam as a solid of pronounced aniseed odour. It crystallised in broad plates (yield, 70%), m. p. 76° (Found: S, 18·0. $C_9H_7ONS$ requires S, 18·1%). p-*Acetylphenylthiocarbamide* formed small, yellow prisms, m. p. 215° (decomp.) (Found: S, 16·8. $C_9H_{10}ON_2S$ requires S, 16·5%). s-*Di*-p-*acetylphenylthiocarbamide* crystallised in sparingly soluble, microscopic crystals, m. p. 198° (Found: S, 10·0. $C_{17}H_{16}O_2N_2S$ requires S, 10·8%).

*Retarded Thiocarbimide Formation.*

In the preparation of the thiocarbimides described below, the mixture was stirred for 30 minutes after the addition of the solution of the amine.

*m*-Nitrobenzonitrile (m. p. 116°; prepared by the nitration of benzonitrile) (14 g.) was warmed with tin (40 g.) and concentrated hydrochloric acid (100 c.c.), the reaction mixture treated with excess of 20% sodium hydroxide, and *m*-cyanoaniline extracted with ether; after recrystallisation from alcohol, this had m. p. 52°.

m-*Cyanophenylthiocarbimide* was obtained as an oil of pungent odour which decomposed on heating to 250°. m-*Cyanophenylthiocarbamide* crystallised in long needles, m. p. 137° (Found: S, 18·0. $C_8H_7N_3S$ requires S, 18·0%). s-*Di*-m-*cyanophenylthiocarbamide*

separated from alcohol in small, cream-coloured crystals, m. p. 144° (Found : S, 11·0. $C_{15}H_{10}N_4S$ requires S, 11·5%).

p-*Cyanophenylthiocarbimide* was obtained by steam-distilling the residue obtained after removal of the chloroform and the excess of thiocarbonyl chloride; on recrystallisation from dilute alcohol it formed glistening, fibrous needles having a strong odour of aniseed, m. p. 45° (Found : S, 19·6. $C_8H_4N_2S$ requires S, 20·0%).

p-*Cyanophenylthiocarbamide* separated from dilute alcohol in prisms, m. p. 169° (Found : S, 18·2%). s-*Di*-p-*cyanophenylthiocarbamide* formed white crystals, m. p. 171° (Found : S, 11·6%).

2 : 5-Dicyanoaniline was prepared as follows : *p*-Dicyanobenzene (prepared from *p*-cyanoaniline by the Sandmeyer reaction) (25 g.) was nitrated with nitric acid (*d* 1·5) at 80° for 20 minutes; a considerable portion of the material was oxidised to benzoquinone. On pouring the nitration product into cold water and extracting the product with ligroin (in which benzoquinone is almost insoluble), 5 g. of the required 2 : 5-dicyanonitrobenzene were obtained, which, on reduction with tin and hydrochloric acid, yielded the dicyanoaniline. On recrystallisation, the amine formed small, brown crystals, m. p. 62°. The yield was 1·5 g.

2 : 5-*Dicyanophenylthiocarbimide*, after recrystallisation from alcohol, retained a strong almond-like odour; it decomposed without melting (Found : S, 17·4. $C_9H_3N_3S$ requires S, 17·3%). 2 : 5-*Dicyanophenylthiocarbamide* separated from alcohol in needles, m. p. 228°.

o-*Bromophenylthiocarbimide* distilled as a colourless oil of pungent odour, b. p. 257°/770 mm. o-*Bromophenylthiocarbamide* separated from alcohol in rosettes of glistening, rhombic prisms, m. p. 125° (Found : S, 14·0. $C_7H_7N_2BrS$ requires S, 13·9%). s-*Di*-o-*bromophenylthiocarbamide* formed long needles, m. p. 157° (Found : S, 9·0. $C_{13}H_{10}N_2Br_2S$ requires S, 8·3%).

2 : 5-*Dibromophenylthiocarbimide* was obtained from 2 : 5-dibromoaniline as a clear oil, b. p. 240°, which formed a glacial mass of needles on cooling; m. p. 17—18° (Found : S, 11·2. $C_7H_3NBr_2S$ requires S, 10·9%). 2 : 5-*Dibromophenylthiocarbamide* formed long needles, m. p. 130° (Found : S, 10·5. $C_7H_6N_2Br_2S$ requires S, 10·3%). s-*Di*-2 : 5-*dibromophenylthiocarbamide*, after two recrystallisations from dilute alcohol, had m. p. 154° (Found : S, 6·0. $C_{13}H_8N_2Br_4S$ requires S, 5·9%).

o-*Iodophenylthiocarbimide* formed long, slender needles having a pungent odour, m. p. 39°. o-*Iodophenylthiocarbamide* separated from alcohol in broad plates, m. p. 157° (Found : S, 11·0. $C_7H_7N_2IS$ requires S, 11·5%). s-*Di*-o-*iodophenylthiocarbamide* separated from dilute alcohol in small, ill-defined crystals, m. p. 164° (decomp.).

m-*Iodophenylthiocarbimide* formed glistening needles, m. p. 46° (Found: S, 12·4. $C_7H_4NIS$ requires S, 12·2%). m-*Iodophenylthiocarbamide* crystallised in white needles, m. p. 160° (decomp.) (Found: S, 11·8%).

3 : 5-*Dibromo*-o-*tolylthiocarbimide*.—The dibromotoluidine (10 g.) was shaken with water and thiocarbonyl chloride, and the mixture steam-distilled; the thiocarbimide was then obtained as a white solid of pungent odour. On recrystallisation from dilute alcohol, it formed a pasty mass of crystals, m. p. about 25°, b. p. 280° (Found: S, 10·0. $C_8H_5NBr_2S$ requires S, 10·5%).

3-*Nitro*-o-*tolylthiocarbimide*.—3-Nitro-*o*-toluidine (10 g.) was refluxed with thiocarbonyl chloride (10 g.) for 10 minutes, and the excess of thiocarbonyl chloride removed in steam. The residue, on recrystallisation from glacial acetic acid, yielded the thiocarbimide in lemon-yellow plates, m. p. 69° (Found: S, 16·1. $C_8H_6O_2N_2S$ requires S, 16·5%).

2-*Nitro*-4-*ethoxyphenylthiocarbimide*.—Ten g. of 2-nitro-*p*-phenetidine were gradually added to a suspension of thiocarbonyl chloride (10 g.) in water (300 c.c.). The thiocarbimide, isolated in the same way as the nitrotolyl compound, crystallised from glacial acetic acid in flat, orange plates, m. p. 78° (Found: S, 14·4. $C_9H_8O_3N_2S$ requires S, 14·3%). 2-*Nitro*-4-*ethoxyphenylthiocarbamide* separated from alcohol in glistening, orange-brown crystals, m. p. 177° (Found: S, 13·0. $C_9H_{11}O_3N_3S$ requires S, 13·3%).

*Thiocarbamide Formation.*

s-*Bis*-3 : 5-*dinitrophenylthiocarbamide*.—3 : 5-Dinitroaniline (10 g.) was shaken with thiocarbonyl chloride (11 g.) in water (150 c.c.) for ½ hour and the excess of thiocarbonyl chloride was then removed in steam. The residue, after several recrystallisations from light petroleum–acetic acid, gave the thiocarbamide in minute, yellow prisms, m. p. 160° (Found: S, 7·5. $C_{13}H_8O_8N_6S$ requires S, 7·8%).

s-*Di*-o-*carboxyphenylthiocarbamide*.—Anthranilic acid (50 g.) was refluxed with thiocarbonyl chloride (50 g.) and water (300 c.c.) for 42 hours, and the excess of chloride removed by steam distillation. The residue was extracted with a large volume of alcohol; the thiocarbamide was then obtained as a granular powder. After several recrystallisations from alcohol (animal charcoal) it was obtained in small crystals, m. p. 300° (decomp.) (Found: S, 10·0. $C_{15}H_{12}O_4N_2S$ requires S, 10·1%).

s-*Di*-p-*acetamidophenylthiocarbamide* was obtained from *p*-aminoacetanilide (20 g.) in the same way as the dicarboxyphenylthiocarbamide, and crystallised in small prisms, m. p. 220° (decomp.) (Found: S, 8·8. $C_{17}H_{18}O_2N_4S$ requires S, 9·3%).

*Inhibition.*

2 : 6-Dichloro-, -dibromo-, -di-iodo-*p*-nitroanilines, 4 : 6-dibromo-*o*-nitroaniline, and 2 : 4 : 6-tribromo-*m*-nitroaniline were all prepared by the methods given in the literature; they were recovered unchanged after treatment with thiocarbonyl chloride and water and identified by m. p. and mixed m. p. determinations. Sulphanilic acid was recovered unchanged after being refluxed with excess of thiocarbonyl chloride and water for 3 hours and identified by its properties, analysis (Found : S, 18·6%), and by the formation of Orange II on diazotisation and coupling with β-naphthol.

In conclusion, we wish to express our gratitude to Professors J. F. Thorpe, F.R.S., and C. K. Ingold, F.R.S., for the interest they have taken in this work and to the Ramsay Memorial Fellowship Trust for a Fellowship awarded to one of us (R. F. H.). Part of the expense has been defrayed by grants from the Research Fund of the Chemical Society and the Dixon Fund of the University of London.

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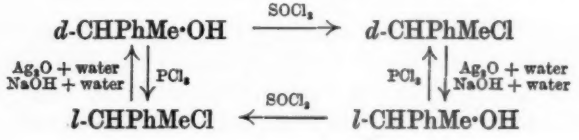
## LXVI.—*Studies on the Walden Inversion. Part XI. Evidence for the Bivalency of Carbon from Some Reactions of α-Chloroethylbenzene. αα′-Diphenyldiethyl Ether.*

By ALLAN MILES WARD.

THE experiments here described were undertaken as a continuation of the method of Part X of this series (J., 1926, 1184) in order to obtain fuller information on the mechanism of the replacement of the halogen in α-chloroethylbenzene; the course of replacement was accordingly followed both by titration and by change of rotation.

The interconversion of the phenylmethylcarbinols was first demonstrated by McKenzie and Clough (J., 1913, **103**, 687); their results may be summarised by the following scheme :



Phosphorus trichloride thus behaves like hydrogen chloride towards phenylmethylcarbinol (compare Pickard and Kenyon, J., 1911, **99**, 71), whilst thionyl chloride behaves differently. In each of the above reactions, with the exception of that of thionyl chloride, racemisation is very considerable.

The displacement of the halogen in α-chloroethylbenzene is here studied in aqueous (20% by volume) ethyl-alcoholic solution at 28·7° and at 50·0°, both alone and also in the presence of sodium hydroxide. The products of reaction in each case are α-phenyldiethyl ether and phenylmethylcarbinol, so that the course of the reaction may be represented thus :

$$\text{(I.)}\quad \text{CHPhMeCl} + \text{EtOH} \longrightarrow \text{CHPhMe·OEt} + \text{HCl}.$$

$$\text{(II.)}\quad \text{CHPhMeCl} + \text{H}_2\text{O} \longrightarrow \text{CHPhMe·OH} + \text{HCl}.$$

The most interesting aspect of these reactions is, however, that the displacement of the halogen proceeds at the same speed whether sodium hydroxide is present in or absent from the solution, and in all cases the velocity coefficients for the reactions, calculated on the basis of a unimolecular reaction, are in good agreement, as shown by the following collected data.

*r*-α-Chloroethylbenzene (approx. *N*/10).
Solvent : Aqueous (20% by volume) ethyl alcohol.

| Exper. | Temp. | Conditions. | *k*. |
|---|---|---|---|
| 3 | 28·7° | Alone | 0·0560 |
| 4 | 28·7 | NaOH (approx. *N*/10) | 0·0561 |
| 5 | 28·7 | NaOH (approx. *N*/5) | 0·0560 |
| 6 | 50·0 | Alone | 0·589 |
| 7 | 50·0 | NaOH (approx. *N*/10) | 0·590 |
| 8 | 50·0 | NaOH (approx. *N*/5) | 0·590 |

The temperature coefficient for 10° is thus 3·02.

These results are analogous to those obtained by Senter (J., 1915, **107**, 908) for the displacement of the halogen in phenylchloroacetic acid in aqueous solution, and for the sodium salt in aqueous and also in sodium hydroxide solutions, where it was found that the displacement reaction in each case is one and the same, namely, the reaction between water and the phenylchloroacetate ion. Results of a similar nature were obtained by Senter and Tucker (J., 1916, **109**, 690) for phenylbromoacetic acid, and they considered that in addition to the reaction

$$\text{CHPhBr·CO}_2' + \text{H}_2\text{O (excess)} \longrightarrow \text{CHPh(OH)·CO}_2' + \text{HBr},$$

water reacted with the undissociated acid also, but about 120 times more slowly. In the present case equations I and II would represent the reactions from the kinetic point of view, but, just as for the reactions between water and the phenylchloroacetate and phenyl-

bromoacetate ions, they fail to provide an explanation for the non-intervention of sodium hydroxide in these reactions.

The velocities of replacement of the halogen in *d*-α-chloroethylbenzene in aqueous ethyl-alcoholic solution in the presence and the absence of sodium hydroxide were also measured by determining the changes in the rotations of the solutions with time at 28·6°. The total change in the rotations of the solutions was small, so that the experimental error is of sufficient relative magnitude to introduce considerable variation in the velocity coefficients when calculated on the basis of a unimolecular reaction according to the formula $k = 2{\cdot}3/t \,.\log_{10}\{(\theta_0 - \theta_\infty)/(\theta_t - \theta_\infty)\}$. The mean of the coefficients in aqueous ethyl alcohol alone is 0·0608, whilst in the presence of sodium hydroxide the mean obtained is 0·0558. These experiments at least confirm the results derived from the titration experiments, namely, that sodium hydroxide is playing no part in the displacement of the halogen.

The displacement of the halogen in β-chloroethylbenzene is in quite striking contrast with the above. Under similar conditions to those employed for α-chloroethylbenzene, the displacement in aqueous alcohol was negligible, whilst in the presence of sodium hydroxide, velocity coefficients agreeing with a bimolecular reaction were obtained; also the displacement of the halogen takes place very much more slowly from β-chloroethylbenzene than from α-chloroethylbenzene. Sodium hydroxide or its ions are therefore playing some essential part in the elimination of the halogen from β-chloroethylbenzene. In other reactions recorded, α- and β-chloroethylbenzenes behave very differently. Thus alcoholic potassium cyanide, followed by hydrolysis, yields β-phenylpropionic acid from β-chloroethylbenzene (Fittig and Kiesow, *Annalen*, 1870, **156**, 245; Schramm, *Monatsh.*, 1887, **8**, 101; Fischer and Schmitz, *Ber.*, 1906, **39**, 2208), whilst from α-chloroethylbenzene under similar conditions α-phenyldiethyl ether is obtained. This ether was first prepared by Thorpe (*Proc. Roy. Soc.*, 1869, **18**, 123) by the interaction of α-bromoethylbenzene and a saturated solution of ammonia in ethyl alcohol, no α-phenylethylamine being produced; it formed also the main product of the reaction between potassium acetate and α-bromoethylbenzene in ethyl-alcoholic solution. The mechanism of the displacement of the halogen from α-chloroethylbenzene would thus appear to be quite different from that in the case of β-chloroethylbenzene.

It was found also in the present experiments that the replacement of the halogen in α-chloroethylbenzene at 50° gives phenylmethylcarbinol only; at 100°, however, the products consist of styrene, phenylmethylcarbinol and αα′-diphenyldiethyl ether; if the boiling

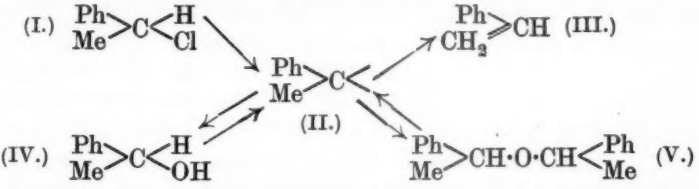
is continued for but 5 minutes, an appreciable amount of the ether is formed. αα′-Diphenyldiethyl ether has previously been prepared, together with phenylmethylcarbinol, by Oddo (*Gazzetta*, 1907, **37**, ii, 360) by the interaction of magnesium methyl iodide and benzaldehyde in the presence of pyridine. Marshall (J., 1914, **105**, 530), in the course of his investigation on the interaction of magnesium methyl iodide and benzaldehyde, obtained a substance which he considered to be αα′-diphenyldiethyl ether, since it did not react with sodium and gave α-chloroethylbenzene on reaction with phosphorus pentachloride. More recently, Wuyts (*Bull. Soc. chim. Belg.*, 1921, **30**, 30), in studying the optical activation of *r*-phenylmethylcarbinol by means of camphorsulphonic acid, found the predominant reaction to be the formation of *l*-αα′-diphenyldiethyl ether with $\alpha_D^{20^\circ} - 1{\cdot}11^\circ$. Descamps (*ibid.*, 1924, **33**, 139) has extended this investigation on the "catalytic dehydration" of phenylmethylcarbinol to αα′-diphenyldiethyl ether. In view of the present results that this ether may be produced readily in the presence of water from α-chloroethylbenzene, and also from phenylmethylcarbinol by boiling with dilute hydrochloric acid, it does not appear justifiable to consider this reaction to be due to a direct dehydration between two molecules of phenylmethylcarbinol.

The only similar example of ether formation known to the author is the case of benzhydrol and diphenylbromomethane. Friedel and Balsohn (*Bull. Soc. chim.*, 1880, **33**, 339) found that diphenylbromomethane, on boiling with water, yielded mainly *s*-tetraphenyldimethyl ether together with a small amount of benzhydrol. This ether had previously been prepared by Linnemann (*Annalen*, 1865, **133**, 14) by prolonged heating of benzhydrol at its boiling point (compare also Thörner and Zincke, *Ber.*, 1878, **11**, 1398; Nef, *Annalen*, 1897, **298**, 234). Nef (*loc. cit.*) found that the displacement of the halogen in diphenylbromomethane by means of water at room temperature gave benzhydrol only, but that *s*-tetraphenyldimethyl ether alone resulted when boiling water was used, and to explain this he assumed that the reactions proceed through a stage involving bivalent carbon by the following mechanism :

$$CHPh_2Br \xrightarrow{-HBr} CPh_2< \begin{cases} \xrightarrow{+H_2O} CHPh_2{\cdot}OH \\ \xrightarrow{CHPh_2{\cdot}OH} (CHPh_2)_2O \end{cases}$$

the addition reactions being exactly analogous to those shown by the *iso*nitriles and the halogenated acetylenes (compare Nef, *Annalen*, 1892, **270**, 267; 1894, **280**, 291; 1895, **287**, 265; 1897, **298**, 202; Lawrie, *Amer. Chem. J.*, 1906, **36**, 489).

In a similar way, the reaction products from α-chloroethylbenzene may be explained by the following scheme :



the first stage of the reaction being the elimination of hydrogen chloride from (I) to yield the highly reactive intermediate phase (II), which then (*a*) undergoes irreversible isomeric change to give styrene (III), (*b*) adds water to give phenylmethylcarbinol (IV), (*c*) adds phenylmethylcarbinol to give αα′-diphenyldiethyl ether (V). The scheme also agrees with the observation that phenylmethylcarbinol, on boiling with *N*/2-hydrochloric acid for 8 hours, yields a mixture of (III), (IV), and (V), and accounts for the similar behaviour of αα′-diphenyldiethyl ether on boiling with *N*/2-hydrochloric acid.

The formation of an intermediate phase involving bivalent carbon is also in accord with the apparent non-intervention of sodium hydroxide as shown in the kinetic results for α-chloroethylbenzene, for if the reaction proceeds by the following stages,

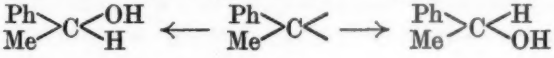
(1) $CHPhMeCl \longrightarrow CPhMe< + HCl$ (slow)

(2) $CPhMe< + \underset{\text{(excess)}}{H_2O} \longrightarrow CHPhMe{\cdot}OH$ (rapid)

(3) $CPhMe< + \underset{\text{(excess)}}{EtOH} \longrightarrow CHPhMe{\cdot}OEt$ (rapid)

then velocity coefficients agreeing with a unimolecular reaction in accordance with stage (1) should be obtained. Further, sodium hydroxide would be expected to play no part in this transformation, for it would be without effect on stage (1), and even should it unite with CPhMe<, such a combination could be only transitory under the conditions of experiment and would lead to the same products as in (2) and (3), and this reaction would be expected to proceed with a velocity comparable with those of (2) and (3). Also by assuming the intermediate phase CPhMe<, the formation of α-phenyldiethyl ether by the reaction between α-chloroethylbenzene and alcoholic ammonia, potassium cyanide or potassium acetate is more readily understood.

The foregoing evidence is thus in accordance with the reaction proceeding through the phase CPhMe<, and it is conceivable that the addition of water to this phase may take place in two ways thus,

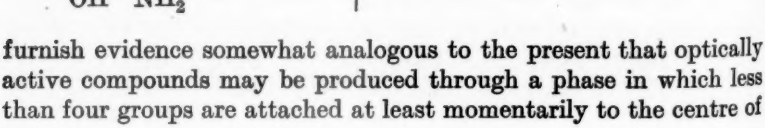


to give rise to a mixture of *d*- and *l*-phenylmethylcarbinols. In general, this may be stated that $CR_1R_2$ will react with a substance XY to give a mixture of $CR_1R_2(X)Y$ and $CR_1R_2(Y)X$, the relative amounts of each isomeride produced depending on the experimental conditions. Nef (*Annalen*, 1904, **335**, 241) has employed this methylene theory to account for the racemisation of hydroxy- and halogen acids and esters of the type $CHRX{\cdot}CO_2H$, and also for the autoracemisation of the halogenosuccinic esters (see Walden, "Optische Umkehrerscheinungen," 1919, V Kapitel), by assuming that the racemisation is due to an equilibrium as follows :

$$CHR(X){\cdot}CO_2H \rightleftharpoons CR(CO_2H)< + HX \rightleftharpoons C(H)RX{\cdot}CO_2H.$$

In a further discussion of these views (*J. Amer. Chem. Soc.*, 1908, **30**, 645), Nef concludes that the four valency units of carbon cannot be regarded as identical, but does not enter into a discussion of the problem of the Walden inversion in connexion with his theory, as he regards the reactions dealt with under this subject as being abnormal in character. Walden (*op. cit.*, p. 182) considers that Nef's views on autoracemisation cannot be correct, since the halogenosuccinic esters, both alone and in solution, are non-electrolytes, and that, were any free halogen acid present, then the conductivity would be appreciable; also no reaction for bromine ion is obtained with silver nitrate solution. The autoracemisation observed by Walden was, however, extremely slow, extending over many years, so that the amount of methylene phase necessary in accordance with Nef's theory must be assumed extremely small.

It might be argued that if the reaction proceeded through an unsaturated phase $CR_1R_2<$, then the resulting compound would of necessity be racemic in nature. There is, however, so far as the author is aware, no experimental evidence to support the view that complete racemisation would ensue. The results of McKenzie, Roger, and Wills (J., 1926, 779) on the reaction between nitrous acid and *l*-β-amino-αα-diphenyl-*n*-propyl alcohol, whereby *d*-methyldeoxybenzoin with $[\alpha]_D^{17^\circ} + 158^\circ$ is produced although the reaction is assumed to proceed through a phase in which but three groups are attached to the centre of asymmetry according to the scheme




furnish evidence somewhat analogous to the present that optically active compounds may be produced through a phase in which less than four groups are attached at least momentarily to the centre of

asymmetry. Phillips (J., 1925, **127**, 2567) had previously discussed the possible free existence of the system $+C\begin{matrix}R_1\\R_2\\R_3\end{matrix}$ in an optically active state in connexion with the problem of the Walden inversion. He considers that such inversions are intimately connected with the withdrawal of two electrons from the valency shell of the atom usually designated as asymmetric; this conception is quite in accord with the mechanism now discussed, for on the basis of the Lewis–Langmuir models the reaction would be represented

$$R_2{:}\overset{R_1}{\underset{:Cl:}{C}}{:}H \longrightarrow R_2{:}\overset{R_1}{C}\cdot + H{:}\ddot{Cl}{:},$$

two electrons being withdrawn from the shell of the asymmetric carbon atom as the first stage (slow) of the reaction, to be followed by the addition reactions (rapid).

The kinetic results on the replacement of the halogen in phenylchloroacetic acid and phenylbromoacetic acid (*loc. cit.*) show the mechanisms of the halogen replacements in these cases to be exactly the same as for α-chloroethylbenzene, so that they would be represented thus:

(1) $CHPhX{\cdot}CO_2' \longrightarrow CPh(CO_2') + HX.$
(2) $CPh(CO_2') + H_2O\ (\text{excess}) \longrightarrow CHPh(CO_2'){\cdot}OH.$

Further, the reaction between water and the *l*-phenylchloroacetate or *l*-phenylbromoacetate ions gives rise to a mixture of *l*- and *d*-mandelic acids, the *l*-acid being in slight excess over the *d*-acid in the case of *l*-phenylchloroacetic acid (McKenzie and Clough, J., 1908, **93**, 811; 1909, **95**, 777), whilst for *l*-phenylbromoacetic acid the reverse holds (McKenzie and Walker, J., 1916, **109**, 1685; Ward, J., 1926, 1190). The mechanisms of the reactions by which the *d*- and *l*-mandelic acids are produced cannot be differentiated (Ward, *loc. cit.*), that is, the mechanisms of the "normal" and "abnormal" reactions are identical from the ordinary kinetic point of view. The production of the mandelic acids by the addition of water in two ways to the intermediate phase, according to the scheme

$$CHPhCl{\cdot}CO_2' \longrightarrow HCl + \begin{matrix}Ph\\CO_2'\end{matrix}\!\!>\!C\!<\!\begin{matrix}\nearrow\ \begin{matrix}Ph\\CO_2'\end{matrix}\!\!>\!C\!<\!\begin{matrix}H\\OH\end{matrix}\\ \searrow\ \begin{matrix}Ph\\CO_2'\end{matrix}\!\!>\!C\!<\!\begin{matrix}OH\\H\end{matrix}\end{matrix}$$

would agree with the observed identity of the two reactions. The similar production of phenylaminoacetic acids of either sign from a

given initial phenylchloroacetic or phenylbromoacetic acid according to the solvent medium used (Senter and Drew, J., 1915, **105**, 638; 1916, **107**, 1091; Senter and Tucker, J., 1918, **113**, 140) would be ascribed to a mechanism of the above type.

## Experimental.

r-*Phenylmethylcarbinol* was prepared by the slow addition during 3—4 hours of 72 g. of benzaldehyde, dissolved in ether, to a vigorously stirred, ice-cooled solution of magnesium methyl iodide, prepared from 142 g. of methyl iodide. After the mixture had remained at room temperature for ½ hour, the additive compound was decomposed with water and dilute acid. The *r*-phenylmethylcarbinol was purified and isolated in the usual way; b. p. 101—102°/20 mm., yield 63 g.

d-*Phenylmethylcarbinol* was obtained by the resolution of the *r*-carbinol by Pickard and Kenyon's method (J., 1911, **99**, 45) and had $\alpha_{5780}^{15°}$ + 22·19° for $l = 0·5$; whence $[\alpha]_{5780}^{15°}$ + 45·0°, compared with Pickard and Kenyon's values $[\alpha]_{D}^{6°}$ + 42·9°, $[\alpha]_{D}^{27°}$ + 42·85°.

r-α-*Chloroethylbenzene* was prepared from *r*-phenylmethylcarbinol by means of thionyl chloride (McKenzie and Clough, J., 1913, **103**, 694); the acidity was almost entirely removed by shaking the product with anhydrous potassium carbonate for a short time and then redistilling it; b. p. 81—82°/17 mm. Results of typical analyses of *r*-α-chloroethylbenzene from different preparations of phenylmethylcarbinol are: Cl, (volumetric), 24·75, 24·98, 24·95, 24·96%; (gravimetric), 25·40, 25·24, 25·18, 25·30%. In the volumetric method, the chlorine was determined by heating a solution of α-chloroethylbenzene in aqueous ethyl alcohol, and titrating the liberated acid with standard alkali until the colour change, with phenolphthalein as indicator, was permanent. For the gravimetric analyses, Stepanow's method was used throughout.

The *r*-α-chloroethylbenzene at first used in these experiments was prepared from phenylmethylcarbinol, obtained by the Grignard reaction from 1 mol. of benzaldehyde and 1 mol. of magnesium methyl iodide. The percentage halogen (gravimetric estimation) in different preparations of this material varied from 23·9 to 24·8 (calc., 25·27%). If the displacement of the halogen was carried out in aqueous (20%) ethyl-alcoholic solution at 28·7°, the final titrations corresponded with Cl = 20·1 to 21·0%, these values being considerably lower than those determined by the gravimetric method. This is not due to an equilibrium of the type $CHPhMeX + H_2O \rightleftharpoons CHPhMe{\cdot}OH + HX$, for under the conditions of experiment phenylmethylcarbinol and hydrogen chloride did not react.

As ordinarily prepared, phenylmethylcarbinol is contaminated with impurities (compare Marshall, J., 1914, **105**, 527; 1915, **107**, 509), which doubtless give chloro-derivatives rendering the α-chloroethylbenzene impure. By preparing the phenylmethylcarbinol as above, with 3 mols. of the Grignard reagent to 2 mols. of benzaldehyde, the values for the percentage halogen in the derived chloro-compound, as shown from the preceding analyses, are in much closer agreement when estimated by the two methods, but in all cases the values found by titration are somewhat lower than those obtained by Stepanow's method. The α-chloroethylbenzene used in the following experiments was prepared by this method.

d-α-*Chloroethylbenzene* was prepared from *d*-phenylmethylcarbinol by McKenzie and Clough's method (*loc. cit.*) and purified as above; b. p. 82—83°/18 mm.; $\alpha^{21^\circ}_{5780} + 26{\cdot}08°$, $l = 0{\cdot}5$, $[\alpha]^{21^\circ}_{5780} + 49{\cdot}07°$ (compare McKenzie and Clough, $[\alpha]_D + 50{\cdot}6°$). The percentages of chlorine, determined by the two methods, were (volumetric) 24·77, (gravimetric) 24·86.

β-*Chloroethylbenzene* prepared from β-phenylethyl alcohol and phosphorus pentachloride (Found: Cl, 25·7. Calc.: Cl, 25·3. Barger, J., 1909, **95**, 2194, found Cl, 25·8%) contained a negligible quantity of hydrogen chloride but an appreciable quantity of phosphorus. Thionyl chloride gave a much purer product: β-Phenylethyl alcohol (25 g.) was slowly added to thionyl chloride (40 g.) at room temperature. Vigorous evolution of hydrogen chloride took place, but the mixture did not become appreciably warm. The reaction mixture was kept for about an hour and then distilled; the product, purified with potassium carbonate, had b. p. 83—84°/14 mm. (yield, 25 g.) (Found: Cl, 25·2%).

α-*Phenylethyl* p-*Nitrobenzoate*.—Phenylmethylcarbinol (1 g.) was dissolved in pyridine (3 g.), and *p*-nitrobenzoyl chloride (1·8 g.) slowly added with cooling. The mixture was kept for 4 hours, treated with excess of dilute sulphuric acid and filtered, and the precipitate was stirred with sodium carbonate solution. The crude ester (2·25 g.) crystallised from aqueous alcohol in pale yellow needles, m.p. 47—48° (Found: equiv. by hydrolysis, 274. $C_{15}H_{13}O_4N$ requires equiv., 271).

*Products of the Reaction of* r-α-*Chloroethylbenzene with Aqueous Ethyl Alcohol*.—Ethyl alcohol (280 c.c.) and water (70 c.c.), both at 50°, were added to *r*-α-chloroethylbenzene (7·5 g.). The solution was maintained at this temperature for 12 hours, the water then removed by means of potassium carbonate, and the alcoholic solution fractionated, 5·8 g. of liquid, b. p. 71—94°/15 mm., being obtained. A mixture of this with pyridine (17 g.) and *p*-nitrobenzoyl chloride (10 g.) was kept for 4 hours, excess of dilute sulphuric

acid was then added, and the pasty product was filtered off, well pressed, and twice washed with some 25 c.c. of ether; 6·2 g. of solid then remained undissolved. The ethereal solution was shaken with the aqueous filtrate, separated, dried, and distilled; α-phenyldiethyl ether (2·55 g.) was then obtained, b. p. 76°/20 mm. (compare Holmberg, *Ber.*, 1912, **45**, 1002, who gives b. p. 71·5—72°/15 mm.) (Found: OEt, 29·5. Calc.: OEt, 30·0%). The residue (6·5 g.) in the distillation flask slowly crystallised. The combined solid products, after treatment with excess of dilute sodium carbonate solution, gave 6·4 g. of crude α-phenylethyl *p*-nitrobenzoate, m. p. 47° after crystallisation from aqueous alcohol.

Similarly, at 28·7°, *r*-α-chloroethylbenzene (5 g.), reacting with ethyl alcohol (280 c.c.) and water (70 c.c.) for 7 days, gave 3·05 g. of product, b. p. 72—90°/13 mm., which, by the above method of separation, yielded 0·85 g. of α-phenyldiethyl ether, b. p. 75°/19 mm. From *r*-α-chloroethylbenzene (5 g.), reacting with ethyl alcohol (280 c.c.) and aqueous 0·967*N*-sodium hydroxide (70 c.c.) at 28·7° for 8 days, 3·45 g. of product, b. p. 72—90°/14 mm., were obtained, from which was separated α-phenyldiethyl ether (1·4 g.), b. p. 71°/15 mm.

In none of these experiments was any evidence obtained of the formation of αα′-diphenyldiethyl ether.

*Reaction between* r-α-*Chloroethylbenzene and Water.*—(a) A mixture of 300 c.c. of water and 20 g. of *r*-α-chloroethylbenzene [Cl, 24·65% (volumetric), 25·27% (gravimetric)] was gently boiled under reflux for 2 hours; the products were then extracted with ether and dried. On distillation the following fractions were obtained: (1) b. p. 52—53°/23 mm., 1·7 g.; (2) b. p. 111—113°/27 mm., 3·7 g.; (3) b. p. 112—160°/23 mm., 1·9 g.; (4) b. p. 167—168°/23 mm., 6·3 g.

Fraction (1) distilled at ordinary pressure at 145—146° (styrene has b. p. 146°/759 mm.), leaving a colourless gum, doubtless metastyrene. Fraction (2), on treatment with thionyl chloride and subsequent purification as in the preparation of *r*-α-chloroethylbenzene, gave a product (3·45 g.), b. p. 87—88°/24 mm. [Found: Cl, 23·9% (volumetric), 25·26% (gravimetric)]; 0·15 g. distilled at 88—170°/24 mm., and the residue was negligible. Fraction (3), treated in the same way as (2), gave 1·45 g., b. p. 85—86°/22 mm. [Found: Cl, 23·95% (volumetric), 24·81% (gravimetric)], and 0·15 g., b. p. 86—150°/22 mm. Fractions (2) and (3) therefore consisted of phenylmethylcarbinol, with possibly some αα′-diphenyldiethyl ether; the low value for the halogen determination by the volumetric method is probably due to the accumulation in these fractions of the substances present in the original material containing the less reactive halogen. Fraction (4), b. p. 167—168°/23 mm.

(Oddo, *loc. cit.*, records the b. p. of αα′-diphenyldiethyl ether as 240—245°/20 mm., undoubtedly in error for 140—145°/20 mm.; Marshall, *loc. cit.*, gives b. p. 148—150°/15 mm.; Wuyts, *loc. cit.*, gives b. p. 156·5°/17 mm.), a clear, colourless liquid which was free from halogen and underwent no change on prolonged standing with sodium, was αα′-diphenyldiethyl ether (Found : C, 85·2; H, 8·0; *M*, cryoscopic in naphthalene, 209. Calc.: C, 85·0; H, 8·0%; *M*, 226).

(b) This experiment was a repetition of (a), except that the time of boiling was 5 minutes only. The fractions obtained were: (1) b. p. 73—76°/20 mm., 6·4 g.; (2) b. p. 85—120°/30 mm., 0·8 g.; (3) b. p. 173—175°/30 mm., 6·2 g. Estimations of chlorine in the fractions gave (1) 18·4%, (2) 11·8%, (3) nil, corresponding with (1) and (2) being mixtures of α-chloroethylbenzene, styrene, and phenylmethylcarbinol, and (3) being αα′-diphenyldiethyl ether.

(c) The replacement of the halogen was carried out at 50°, a stirred mixture of *r*-α-chloroethylbenzene (25 g.) and water (400 c.c.) being warmed for 12 hours. The product (19 g.) had b. p. 99—105°/20 mm., and therefore was phenylmethylcarbinol alone; some 0·5 g. of liquid remained in the distilling flask.

*Reaction between Phenylmethylcarbinol and Water.*—*r*-Phenylmethylcarbinol (10 g.) was heated with water (160 c.c.) at 100° for 8 hours. The bulk (7·5 g.) of the product, b. p. 104—106°/24 mm., was unchanged phenylmethylcarbinol; a second fraction (0·8 g.) had b. p. 106—120°/24 mm.

*Reaction between Phenylmethylcarbinol and Hydrochloric Acid.*—*r*-Phenylmethylcarbinol (20 g.) was heated with hydrochloric acid (320 c.c.; approx. *N*/2) at 100° for 8 hours. The products were (1) styrene, b. p. 54—58°/24 mm., 1·2 g., (2) phenylmethylcarbinol, b. p. 106—109°/24 mm., 2·5 g., (3) αα′-diphenyldiethyl ether, b. p. 163—165°/21 mm., 9·45 g.

*Reaction between αα′-Diphenyldiethyl Ether and Hydrochloric Acid.*—The ether (15 g.) was heated under the conditions of the preceding experiment. The products were: (1) styrene, b. p. 47—50°/22 mm., 0·35 g., (2) phenylmethylcarbinol, b. p. 118—126°/31 mm., 2·0 g., (3) αα′-diphenyldiethyl ether, b. p. 175—177°/31 mm., 8·95 g.

### *Kinetic Experiments.*

In the following experiments the solvent medium employed throughout was aqueous (20% by volume) ethyl alcohol. The ethyl alcohol used was commercial absolute alcohol, dried by refluxing and distilling over quick-lime. In preparing the solution the substance under investigation was dissolved in ethyl alcohol, the measured volumes of water, hydrochloric acid, or sodium hydroxide added, and the solution made up to volume with ethyl alcohol,

all the reactants being at the temperature of experiment. The amounts of carbinol and chloro-compounds used, and also the concentrations of added hydrogen chloride or sodium hydroxide, are expressed in mols. per litre; all titrations are referred to 20 c.c. of the solution against sodium hydroxide ($N/10$) or alcoholic benzoic acid ($N/10$), the actual experimental figures being converted to this basis. In all titration experiments, phenolphthalein was used as indicator. Unless otherwise stated, the values of $k$ are calculated from the formula $k = 2{\cdot}3/t.\ \log_{10}\{a/(a-x)\}$ for a unimolecular reaction.

(1) *r*-Phenylmethylcarbinol, 0·0983; hydrogen chloride, 0·0935; temp. 28·5°.

| Time (hrs.) ... | 0·27 | 1·1 | 24·7 | 48 | 96 | 216 |
|---|---|---|---|---|---|---|
| Titre ..... | 18·60 | 18·67 | 18·62 | 18·71 | 18·78 | 18·78 |

(2) *r*-Phenylmethylcarbinol, 0·1211; hydrogen chloride, 0·1870; temp. 28·5°.

| Time (hrs.) ..... | 2 | 72 | 96 | 120 | 144 |
|---|---|---|---|---|---|
| Titre ..... | 37·38 | 37·39 | 37·43 | 37·32 | 37·69 |

(3) *r*-α-Chloroethylbenzene, 0·0906; temp. 28·7°.

| Time (hrs.). | Titre. | $k$. | Time (hrs.). | Titre. | $k$. |
|---|---|---|---|---|---|
| 0·1 | 0·185 | — | 34·1 | 15·41 | 0·0569 |
| 3·1 | 2·93 | 0·0557 | 55·35 | 17·09 | 0·0541 |
| 6·1 | 5·24 | 0·0557 | 144 | 17·81 | — |
| 10·1 | 7·92 | 0·0570 | 192 | 17·97 | — |
| 23·1 | 13·17 | 0·0568 | 240 | 17·98 | — |

(4) *r*-α-Chloroethylbenzene, 0·0849; sodium hydroxide, 0·0941; temp. 28·7°.

| Time (hrs.). | Titre. | $k$. | Time (hrs.). | Titre. | $k$. |
|---|---|---|---|---|---|
| 0·1 | 18·69 | — | 30·1 | 4·93 | 0·0566 |
| 3·1 | 16·13 | 0·0549 | 54·1 | 2·62 | 0·0571 |
| 7·1 | 13·29 | 0·0552 | 122·1 | 1·86 | — |
| 10·6 | 11·18 | 0·0561 | 171·1 | 1·85 | — |

(5) *r*-α-Chloroethylbenzene, 0·0890; sodium hydroxide, 0·1882; temp. 28·7°.

| Time (hrs.). | Titre. | $k$. | Time (hrs.) | Titre. | $k$. |
|---|---|---|---|---|---|
| 0·1 | 37·65 | — | 54·1 | 20·66 | 0·0565 |
| 3·1 | 34·84 | 0·0569 | 120·1 | 19·83 | — |
| 7·1 | 31·91 | 0·0554 | 144·1 | 19·83 | — |
| 11·1 | 29·44 | 0·0551 | 168·1 | 19·82 | — |
| 30·1 | 23·09 | 0·0565 | | | |

The mean values of the velocity coefficients obtained at 50·0°, as in (3), (4) and (5), are summarised below.

| Exper. | *r*-α-Chloroethylbenzene. | Sodium hydroxide. | $k$. |
|---|---|---|---|
| (6) | 0·0903 mol./l. | — | 0·589 |
| (7) | 0·0833 | 0·1025 mol./l. | 0·590 |
| (8) | 0·0924 | 0·2050 | 0·590 |

(9) *d*-α-Chloroethylbenzene, 0·1071; samples were withdrawn at the times shown, and their rotations determined in a 2 dm.-tube for the yellow mercury line; temp. 28·6°.

| Time (hrs.). | $\alpha^{28\cdot6°}_{5780}$. | *k*. | Time (hrs.). | $\alpha^{28\cdot6°}_{5780}$. | *k*. |
|---|---|---|---|---|---|
| 0·19 | + 1·30° | — | 27·00 | − 0·09° | 0·0598 |
| 1·17 | + 1·20 | 0·0603 | 30·64 | − 0·17 | 0·0611 |
| 3·06 | + 1·02 | 0·0610 | 48·94 | − 0·33 | 0·0566 |
| 5·07 | + 0·85 | 0·0612 | 6 days | − 0·39 | — |
| 7·02 | + 0·69 | 0·0631 | 10 ,, | − 0·43 | — |
| 9·06 | + 0·56 | 0·0624 | 27 ,, | − 0·43 | — |
| 11·93 | + 0·40 | 0·0619 | 159 ,, | − 0·44 | — |

(10) *d*-α-Chloroethylbenzene, 0·0929; sodium hydroxide, 0·1092. The solution was turbid and was filtered before the measurements were made. The initial rotation ($t = 0·18$ hr.) was $\alpha^{28\cdot6°}_{5780}$ + 0·85°, and the final value ($t = 120$ hrs.) was $\alpha^{28\cdot6°}_{5780}$ − 0·36°, for $l = 2$. The individual values of *k* varied from 0·0539 to 0·0582, giving a mean of 0·0558.

(11) β-Chloromethylbenzene, 0·0996; temp. 28·9°.

| Time (days) ... | 0 | 1 | 5 | 11 | 22 | 55 |
|---|---|---|---|---|---|---|
| Titre ..... | 0·11 | 0·09 | 0·12 | 0·22 | 0·25 | 0·33 |

(12) β-Chloroethylbenzene, 0·0975; sodium hydroxide, 0·1858; temp. 28·9°.

| Time (days). | Titre. | *k*. | Time (days). | Titre. | *k*. |
|---|---|---|---|---|---|
| 0·0 | 37·16 | — | 4 | 33·38 | 0·0016 |
| 0·5 | 36·40 | 0·0022 | 8 | 30·30 | 0·0016 |
| 1·07 | 35·88 | 0·0018 | 19 | 25·90 | 0·0015 |
| 2·01 | 35·00 | 0·0016 | 26 | 23·98 | 0·0015 |
| 3·02 | 34·10 | 0·0016 | 52 | 19·94 | 0·0016 |

*k* is equal to $\frac{2·3}{(b-a)t}\log_{10}\frac{a(b-x)}{b(a-x)}$, *t* being measured in days, *a*, *b* and *x* in c.c. of *N*/10-acid.

(13) β-Chloroethylbenzene, 0·0917; sodium hydroxide, 0·0929; temp. 28·9°.

| Time (days). | Titre. | *k*. | Time (days). | Titre. | *k*. |
|---|---|---|---|---|---|
| 0·01 | 18·48 | — | 7 | 14·99 | 0·0018 |
| 0·40 | 18·35 | 0·0010 | 18 | 11·84 | 0·0017 |
| 1·00 | 17·79 | 0·0022 | 25 | 10·26 | 0·0017 |
| 2·13 | 17·34 | 0·0017 | 51 | 6·70 | 0·0019 |
| 3·04 | 16·95 | 0·0016 | | | |

The formula for a bimolecular reaction where $a = b$, namely, $k = x/ta(a-x)$, was used.

*Summary.*

(1) The displacement of the halogen in *r*-α-chloroethylbenzene in aqueous ethyl-alcoholic solution alone and also in the presence of sodium hydroxide at 28·7° and at 50·0° yields a mixture of phenyl-

methylcarbinol and α-phenyldiethyl ether; the velocity coefficient obtained in each case is that of a unimolecular reaction, the sodium hydroxide or its ions playing no part in the halogen displacement.

(2) This result is confirmed by a calculation of the velocity coefficients from observations on the change in the rotation of solutions of *d*-α-chloroethylbenzene under comparable conditions.

(3) The displacement of the halogen in β-chloroethylbenzene is in marked contrast to the above; in aqueous ethyl-alcoholic solution the displacement is negligibly slow; in the presence of sodium hydroxide, velocity coefficients of a bimolecular reaction are obtained but the halogen displacement proceeds much more slowly than in the case of α-chloroethylbenzene.

(4) *r*-α-Chloroethylbenzene, on boiling with water, yields mainly αα′-diphenyldiethyl ether, together with styrene and phenylmethylcarbinol. The same products are obtained on boiling phenylmethylcarbinol with *N*/2-hydrochloric acid, and also by submitting αα′-diphenyldiethyl ether to similar treatment.

(5) The experimental evidence under (1), (2), and (4) is in accordance with the reaction proceeding through a phase CPhMe<, in which but two groups are momentarily attached to carbon.

(6) The mechanism under (5) is discussed in connexion with the Walden inversion.

The author wishes to express his thanks to Drs. Senter and Barrow for their valued interest in this research, and also to the Department of Scientific and Industrial Research for a maintenance grant during a part of the time occupied in carrying it out.

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## LXVII.—*Acid and Salt Effects in Catalysed Reactions. Part VI.* The Early Stages of an Auto-catalysed Reaction. Generalised Form of the Simple Auto-catalytic Catenary.*

By HARRY MEDFORTH DAWSON.

THE investigation of the auto-catalytic reaction between acetone and iodine (Dawson and Powis, J., 1912, **101**, 1503) showed that when the concentration of the acetone is constant, the course of

* Paper V of this series is published in the *Proc. Leeds Phil. Lit. Soc.*, 1926, **1**, 108, under the title "Isohydric Solutions and the Velocity of Chemical Change."

the reaction can be represented very accurately by the simplest possible type of auto-catalytic equation, namely, $dx/dt = kx$, where $x$, the observed fall in the iodine concentration after time $t$, affords a measure of the concentration of the hydriodic acid produced; if not too small, this may be taken to represent the hydrogen-ion concentration.

With an acetone concentration of 20 c.c. per litre ($0{\cdot}272M$), the time required at 25° to reach the stage at which the value of $x$ can be measured by titration with $0{\cdot}01N$-thiosulphate is about 3 days. During this period, the course of the reaction cannot be followed by any direct method,* and one of the objects of this paper is to show how the nature of the changes taking place in the early stages of the reaction may be elucidated by an indirect method.

On extrapolating the straight line obtained by plotting $\log x$ against $t$, Dawson and Powis obtained a value of $x$ for $t = 0$, which represented the apparent initial hydrogen-ion concentration when it was assumed that the reaction proceeded in its early stages in accordance with the equation found to represent accurately the experimental observations for the later stages. This empirically derived value of $x$ will be referred to in this paper by "$x_0$." It represents the constant in the integrated form of the differential equation, which may therefore be written $k = 1/t \,.\, \log_e x/"x_0"$.

The experimental data showed that "$x_0$" is reproducible within narrow limits, but its relatively high value seemed to preclude the possibility that "$x_0$" could correspond with the true initial hydrogen-ion concentration of the solution. This view was supported by the fact that the addition of small quantities of alkali to the original solution made no difference in the value obtained for "$x_0$." On the other hand, it was found that the value of "$x_0$" is reduced by the addition of small quantities of hydrochloric acid and that it becomes equal to zero when the amount of added acid is sufficient to give approximately a $10^{-4}N$-solution.

More recent experiments (Dawson and Carter, J., 1926, 2282) have shown that the hydroxyl ion is a very active catalyst for the acetone–iodine reaction, and it therefore seemed very probable that the participation of hydroxyl ions in the early stages of the auto-catalytic change might be responsible for the above behaviour. It will be shown that this assumption is quite in accordance with the facts and that the initial stage of the auto-catalysed reaction is very different in character from the later stages. The analysis to be described is of particular interest in that it illustrates the possibility of obtaining detailed information relative to the mechanism

* Conductivity measurements are not applicable and preliminary attempts to measure the hydrogen potential did not appear to be hopeful.

of a reaction at a stage which is inaccessible to direct experimental observation.

*The Hydrogen-ion Concentration of the Original Solution.*

In addition to acetone and iodine, the original solution contained potassium iodide, added in the molecular ratio $KI : I_2 = 2 : 1$ to dissolve the requisite amount of iodine. Since hydrogen ions are produced by ionisation of the solvent and also by hydrolysis of the iodine, it is obviously necessary to inquire under what conditions the hydrogen ions produced by the reaction and measured by $x$ may be taken as a measure of the total hydrogen-ion concentration. It will be shown that this condition is attained when $x$ reaches a value which may be placed at about $2 \times 10^{-6}$, and that, from the kinetic standpoint, it is not of any great importance to know the precise value of the hydrogen-ion concentration of the original solution provided that it is not greater than this limiting value.

So far as the hydrogen ions produced by the solvent are concerned, it follows at once from the equation

$$[H^+] \cdot (x + [H^+]) = 10^{-14}$$

that $[H^+]$ may be entirely neglected when $x = 2 \times 10^{-6}$.

In regard to the hydrogen ions produced by hydrolysis of the iodine, consideration must be given to the equilibria

$$I_2 + I^- \rightleftarrows I_3^-$$

and

$$I_2 + H_2O \rightleftarrows H^+ + I^- + HIO.$$

The constant characteristic of the first equilibrium $K_1 = [I_2] \cdot [I^-]/[I_3^-]$ is equal to $1{\cdot}38 \times 10^{-3}$ (Jakowkin, *Z. physikal. Chem.*, 1896, **20**, 19). For the second, the value of $K_2 = [H^+] \cdot [I^-] \cdot [HIO]/[I_2]$, according to measurements of the electrical conductivity of a saturated solution of iodine in pure water, is equal to $0{\cdot}6 \times 10^{-12}$ (Bray, *J. Amer. Chem. Soc.*, 1910, **32**, 932). The value of this constant is not nearly so trustworthy as $K_1$, but its accuracy is probably quite sufficient for the present purpose.

In the auto-catalytic experiments, the concentrations of the iodine and potassium iodide were for the most part 0·004 and 0·008 mol. per litre, respectively. Introducing these values into the equation for $K_1$, it may be shown that the ratio $[I_2]/[I^-]$ is approximately equal to 0·18. This ratio remains constant in the initial stage of the auto-catalytic change, and by reference to the equation for $K_2$, since $[H^+] = [HIO]$, it follows that the initial hydrogen-ion concentration due to iodine hydrolysis is given by $[H^+]_0 = \sqrt{K_2 \cdot [I_2]/[I^-]} = 3{\cdot}3 \times 10^{-7}$. When $x$ mols. of hydriodic acid have been produced by the acetone reaction, the concentration

$[H^+]$ of the hydrogen ions resulting from iodine hydrolysis is given by

$$[H^+] \cdot (x + [H^+]) = (3{\cdot}3 \times 10^{-7})^2,$$

from which, if $x = 2 \times 10^{-6}$, the value obtained for $[H^+]$ is $0{\cdot}5 \times 10^{-7}$. In other words, the hydrogen ions formed by iodine hydrolysis represent only 2·5% of the total when $x = 2 \times 10^{-6}$ and may therefore without serious error be left out of account.

The foregoing analysis is necessarily antecedent to the dynamic considerations which follow. The practical outcome of it is that the total hydrogen-ion concentration throughout the initial period is determined by the concentration ($x$) of the auto-catalytically produced hydrogen ion. The interval for which this is not true is negligibly small.

*Dynamics of the Auto-catalysed Reaction.*

In accordance with the assumption that the course of the auto-catalytic change is determined by the joint action of the hydrogen and hydroxyl ions, we have

$$v = v_h + v_{OH} = k_h[H^+] + k_{OH}[OH^-] \quad . \quad . \quad . \quad (1)$$

In conformity with the preceding analysis and the equation $[H^+] \cdot [OH^-] = K_w$, equation (1) may be written

$$v = dx/dt = k_h x + k_{OH} \cdot K_w/x \quad . \quad . \quad . \quad . \quad (2)$$

The speed of the reaction at any particular moment cannot of course be directly measured, but by integration of (2) an equation is obtained which expresses the time required for the reaction to proceed to any point represented by $x$. This takes the form

$$t = 1/2k_h \cdot \log_e (k_h x^2 + k_{OH} \cdot K_w) + \text{const.} \quad . \quad . \quad (3)$$

or, if $x = x_0$ (the true initial hydrogen-ion concentration) when $t = 0$,

$$t = 1/2k_h \cdot \log_e (k_h x^2 + k_{OH} \cdot K_w)/(k_h x_0^2 + k_{OH} \cdot K_w) \quad . \quad (4)$$

By differentiation of (2) we obtain

$$dv/dx = k_h - k_{OH} \cdot K_w/x^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

from which it is apparent that the velocity passes through a minimum when

$$x = x_i = \sqrt{k_{OH} \cdot K_w/k_h} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This minimum velocity is given by

$$v_i = 2\sqrt{k_{OH} \cdot K_w \cdot k_h} = 2k_h \cdot x_i \quad . \quad . \quad . \quad . \quad (7)$$

Substituting in (4) the value of $k_{OH} \cdot K_w$ given by (6), we obtain

$$t = 1/2k_h \cdot \log_e (x^2 + x_i^2)/(x_0^2 + x_i^2) \quad . \quad . \quad (8)$$

The time required for the auto-catalytic change to proceed to any stage measured by a fall in iodine concentration equal to $x$ may thus be calculated from (4) or (8).

If $x$ is large and $x_0$ small relatively to $x_i$, these equations may be written

$$t = 1/2k_h \,.\, \log_e k_h x^2/k_{OH} \,.\, K_w \quad . \quad . \quad . \quad . \quad . \quad (4A)$$

and

$$t = 1/2k_h \,.\, \log_e x^2/x_i^2 = 1/k_h \,.\, \log_e x/x_i \quad . \quad . \quad (8A)$$

respectively. If $x_i$ in equation (8A) is replaced by "$x_0$," it becomes identical with the empirical equation used by Dawson and Powis. It is thus possible to give a simple interpretation to the empirical quantity "$x_0$" which was introduced as a measure of the apparent initial acidity in conformity with the simple hydrogen-ion theory of catalysis. It is indeed evident that "$x_0$" is a measure of the hydrogen-ion concentration at the point of minimum velocity. We have therefore

$$\text{"}x_0\text{"} = x_i = \sqrt{k_{OH} \,.\, K_w/k_h} \quad . \quad . \quad . \quad . \quad (9)$$

and since $k_h$, $K_w$, and "$x_0$" are known, this relation may be used for the determination of $k_{OH}$. For "$x_0$" the mean value of four experiments recorded by Dawson and Powis is $2{\cdot}07 \times 10^{-5}$, and since $k_h = 4{\cdot}68 \times 10^{-4}$ * and $K_w = 10^{-14}$, we obtain

$$k_{OH} = 19{\cdot}9 \text{ (say 20)}.$$

According to this result, the activity of the hydroxyl ion is about 43,000 times that of the hydrogen ion.

An approximate evaluation of $k_{OH}$ was attempted by Dawson and Carter from observations on the catalytic activity of mixtures of acetic acid and sodium acetate belonging to the series $(0{\cdot}2 - x)CH_3{\cdot}CO_2H + xCH_3CO_2Na$, from which $k_{OH} = 10$. There can be no doubt that very much greater weight must be attached to the value given by the auto-catalytic experiments.

In reference to equations (8) and (8A) it may be noted that the experimental constancy of "$x_0$" justifies the conclusion that the true initial hydrogen-ion concentration ($x_0$) of the acetone–iodine-iodide solution is so small compared with that corresponding with minimum velocity ($x_i$) that $x_0^2$ may be neglected in comparison with $x_i^2$.

From equation (8) the time required to reach the value $x = 2 \times 10^{-6}$ (see pp. 460, 461) is found to be $t = 9{\cdot}7$ minutes. This is very small compared with the time which elapses before the reaction reaches the measurable stage (not less than 3 days), and it follows

* The coefficient given by Dawson and Powis is 0·1035 (time in hours, acetone concentration = 1$M$); when time is expressed in minutes, and the coefficient is referred to 20 c.c. of acetone per litre, it has the value $4{\cdot}68 \times 10^{-4}$.

that the commencement of the reaction could be identified without appreciable error with the time at which the total hydrogen-ion concentration begins to be determined by the auto-catalytically produced hydrogen ion.

It is of interest to note that the total time of reaction given by (8) may be divided into two periods, the first ($t_1$) representing the time required for the attainment of minimum velocity, whilst the second ($t_2$) represents the period in which the velocity of the reaction is continually increasing. The values of $t_1$ and $t_2$ are given by

$$t_1 = 1/2k_h \,.\, \log_e (x_i^2 + x_i^2)/x_i^2 = 1/2k_h \,.\, \log_e 2 \,. \quad . \quad (10)$$

$$t_2 = 1/2k_h \,.\, \log_e (x^2 + x_i^2)/2x_i^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (10A)$$

Substituting $k_h = 4{\cdot}68 \times 10^{-4}$, equation (10) shows that the maximum time required for the attainment of minimum velocity is 12 hrs. 20 minutes. If the $p_H$ value of the original solution is greater than 6, the actual time will differ from the maximum time by less than 5 minutes, and the actual and maximum times may therefore be regarded as identical.

We may now proceed to make a comparison of the time observed for the reaction to proceed to a given point in the measurable stage with that calculated from the general equation (8). Provided that the point in question lies within the measured region, its actual value is not of any great importance. It may be conveniently taken as the point corresponding with $x = 10^{-3}$ ($p_H = 3$). When a 25 c.c. sample of the solution is titrated with 0·01*N*-thiosulphate, this corresponds with a fall of 5·0 c.c. in the amount of thiosulphate required, a quantity which can be measured without sensible error. The observed times are those derived from the straight-line plots of log $x$ against $t$. The relevant data are given in Table I. In all the experiments, with one exception, the original solution contained 20 c.c. of acetone, 0·004 mols. of iodine and 0·008 mols. of potassium iodide per litre. In Expt. 3, the concentrations of the iodine and iodide were respectively 0·005 and 0·01. When alkali or acid was added, this is shown in column 2.

TABLE I.

| Expt. No. | Substances added to the iodine–iodide solution. | $t_{obs.}$ (hrs.). | $t_{cal.}$ (hrs.). |
|---|---|---|---|
| 1 | None. | 133 | 138 |
| 2 | None. | 135·5 | 138 |
| 3 | None. | 141 | 138 |
| 4 | $4 \times 10^{-5}$ *N*-NaOH | 138 | 138 |
| 5 | $2 \times 10^{-5}$ *N*-HCl | 121 | 126 |
| 6 | $4 \times 10^{-5}$ *N*-HCl | 107 | 112 |
| 7 | $8 \times 10^{-5}$ *N*-HCl | 88 | 89 |

The agreement between the observed and the calculated time intervals is such as to justify the conclusion that the course of the

auto-catalytic change is in accordance with the views which have been put forward.

In order to facilitate the visualisation of the early stages of the reaction, the appended diagram (upper curve) shows the variation of $\log x$ with $t$. In the measurable stage, the relation between these is linear, but in accordance with the equation

$$d \log x/dt = k_h + k_{OH} \cdot K_w/x^2 \quad . \quad . \quad . \quad . \quad (11)$$

[an alternative form of equation (2)] the slope of the initial portion of the curve increases continuously as $x$ diminishes. The lower curve in the diagram shows the dependence of the reaction velocity on the time. In drawing this curve, corresponding values of $x$ and $t$ were derived from equation (8) on the assumption that $x_0$ is negligibly small, and the required velocities were then calculated from equation (2). The relevant numbers are shown in Table II.

FIG. 1.

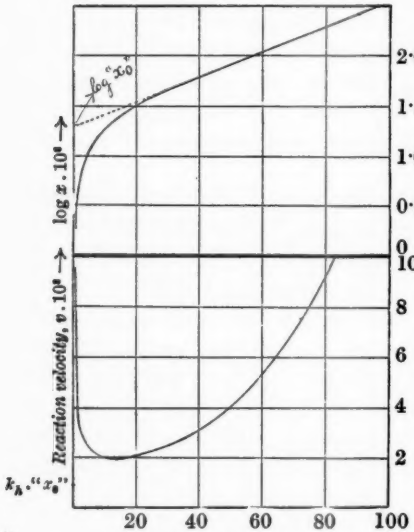


*Diagram showing* $\log x - t$ *and* $v - t$ *curves.*

In the region of actual measurement, the velocity–time curve is exponential and corresponds with the equation $v = k_h \cdot x_i \cdot e^{k_h t}$, which represents the integrated form of $dx/dt = k_h x$ when the value of $x$ for $t = 0$ is made equal to $x_i = "x_0."$

A further relation which characterises the velocity–time curve may be noted. When $k_{OH} \cdot K_w$ is replaced by $k_h x_i^2$, equation (11) assumes the form

$$d \log x/dt = k_h(x^2 + x_i^2)/x^2 \quad . \quad . \quad . \quad . \quad (12)$$

and from (5) we obtain

$$dv/d \log x = k_h(x^2 - x_i^2)/x \quad . \quad . \quad . \quad . \quad (13)$$

Combining these equations, there results

$$dv/dt = k_h^2(x^4 - x_i^4)/x^3 \quad . \quad . \quad . \quad . \quad (14)$$

which, for relatively large values of $x$, takes the form

$$dv/dt = k_h^2 x \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which may, of course, be obtained directly from $v = k_h \cdot "x_0" \cdot e^{k_h t}$.

TABLE II.

| $x \cdot 10_6$. | $p_H$. | $t$ (mins.). | $v \cdot 10^8$. | $x \cdot 10^6$. | $p_H$. | $t$ (mins.). | $v \cdot 10^8$. |
|---|---|---|---|---|---|---|---|
| 2 | 5·70 | 9·7 | 10·1 | 50 | 4·30 | 2055 | 2·74 |
| 4 | 5·40 | 39·1 | 5·19 | 100 | 4·00 | 3410 | 4·88 |
| 6 | 5·22 | 86·6 | 3·62 | 200 | 3·70 | 4860 | 9·46 |
| 8 | 5·10 | 149 | 2·88 | 500 | 3·30 | 6820 | 23·5 |
| 10 | 5·00 | 225 | 2·47 | 1000 | 3·00 | 8290 | 46·8 |
| 20·7 | 4·68 | 740 | 1·94 | | | | |

The asymmetry of the velocity–time curve, as shown by the diagram, is at once apparent from equation (14).

*Generalised Form of the Auto-catalytic Catenary.*

In previous papers (Dawson and Dean, J., 1926, 2872; Dawson and Hoskins, J., 1926, 3166), it was shown that the catalytic effects resulting from the joint action of the positive and negative ions produced by the ionisation of an acid of constant concentration can be represented by a catenary curve when the reaction velocity is plotted against $p_H$. The curve connecting the velocity of the auto-catalytic change discussed in this paper with $\log x$ (or $p_H$) is of exactly the same type [compare equation (5)]. In reference to the auto-catalytic catenary, it is to be noted, however, that this represents the *actual* course of the chemical change. The movement of an index point along the catenary corresponds *de facto* with the continuously successive stages of the auto-catalysed reaction.

Following the procedure described in the derivation of the general catalytic catenary (Dawson, this vol., p. 215), and expressing the auto-catalytic reaction velocity in terms of the minimum velocity ($r = v/v_i$), and the hydrogen-ion concentration in terms of its value at the point of minimum velocity ($n = x/x_i$), it may be shown that the reduced velocity $r$ at any stage of the reaction is given by

$$r = \tfrac{1}{2}(n + 1/n) = \tfrac{1}{2}(e^h + e^{-h}) = \cosh h \quad . \quad . \quad (16)$$

where $h$ is the natural logarithm of the reduced hydrogen-ion concentration, $n$.

Since this equation contains no specific constants, it represents a generalised form of auto-catalytic catenary which should be applicable to all auto-catalysed reactions of the type under discussion. It should therefore be independent of the nature of the particular substances taking part in the change, of the temperature, and of the solvent.

*Summary.*

It has been shown that the phenomena associated with the auto-catalytic reaction of acetone with iodine in aqueous solution can be interpreted in terms of the joint catalytic activity of the hydrogen and hydroxyl ions.

Equations have been derived which show that the reaction velocity falls to a minimum and then increases.

The time calculated for the reaction to proceed to any given point is in close agreement with experiment.

The constant which in terms of the simple hydrogen-ion theory appears to measure the initial hydrogen-ion concentration is found to represent the actual hydrogen-ion concentration at the point of minimum velocity.

The value of this constant affords a means of determining the catalytic coefficient of the hydroxyl ion.

It is further shown that the auto-catalytic catenary obtained by plotting $v$ against $p_H$ can be put into a general form by expressing the velocity and hydrogen-ion concentration in terms of those values which characterise the point of minimum velocity. The actual course of the auto-catalytic change is then given by $r = \cosh h$, where $r$ is the reduced velocity and $h$ is the natural logarithm of the reduced hydrogen-ion concentration.

THE UNIVERSITY, LEEDS. [*Received, January 4th*, 1927.]

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## LXVIII.—*The Partition of Hydrogen Chloride between Water and Benzene.*

By RICHARD WINTON KNIGHT and CYRIL NORMAN HINSHELWOOD.

THE well-known method of determining the state of substances in solution by partition experiments can be utilised to throw light upon the state of strong electrolytes dissolved in water.

Debye and Hückel have shown that when the apparent degree of dissociation of such an electrolyte is corrected for the effect of the inter-ionic forces on the conductivity and on the osmotic pressure, the result is nearly unity for solutions of moderate concentration. This is referred to as complete dissociation. The result does not prove the absolute non-existence of un-ionised molecules, but simply shows that their concentration, if they do exist, is very much smaller than was supposed before the proper corrections were introduced.

There is, on the other hand, positive evidence for the existence of un-ionised molecules, if only in extremely small concentration, wherever there is a definite partition between water and some non-polar solvent. Little work has been done on the partition of strong electrolytes, because it is difficult to find one having a sufficiently great solubility in a suitable non-polar solvent, a fact which itself indicates the reluctance with which un-ionised molecules are formed. Among the most important papers bearing on the subject are those

of Hill (*J. Amer. Chem. Soc.*, 1921, **43**, 254), on the partition of silver perchlorate between water and benzene, Rothmund and Drucker (*Z. physikal. Chem.*, 1903, **46**, 827), on picric acid and the same two solvents, and Cavanagh (*Proc. Roy. Soc.*, 1924, [*A*], **106**, 243), on the partition of lithium chloride between water and amyl alcohol.

At sufficiently high concentrations aqueous solutions of hydrogen chloride have a considerable partial pressure of gaseous hydrogen chloride, showing that un-ionised molecules must exist in solution. It seemed likely that further information would be obtained by studying the partition of hydrogen chloride between water and benzene up to concentrations as high as possible. The work now described does not aim at establishing standard values for the various solubilities, but only at showing the general nature of the partition relationships. Nevertheless, it seems to show quite clearly that there is a definite equilibrium in water between ionised and un-ionised hydrogen chloride. Up to a concentration of about 10*N* there is only a very small proportion of un-ionised molecules, in accordance with the results of Debye and Hückel, a fact which can also be seen from the vapour-pressure results. Above about 15*N*, however, the proportion of un-ionised molecules becomes very considerable, and in the region 15—20*N* there is a roughly constant partition coefficient, indicating that the state of the greater part of the hydrogen chloride in the water is the same as its state in the benzene.

No information could be found about the solubility of hydrogen chloride in benzene. This was therefore determined. The solubility in water is given in most standard works, but all data appear to rest upon the original determination of Roscoe and Dittmar (J., 1860, **12**, 128). The value was therefore re-determined at 20° by a different method.

The benzene was prepared from the purest "Analytical Reagent." It was first extracted with pure concentrated sulphuric acid, after which it showed no trace of the indophenin reaction. It was then fractionated through a 6-foot column and collected in large flasks provided with syphons, all corks used being covered with pure tinfoil. It was subsequently twice purified by freezing. The final m. p.'s of four portions were 5·48°, 5·48°, 5·47°, and 5·47° (correct to 0·02°). (Sidgwick, J., 1920, **117**, 1340, gives 5·49° for pure benzene.)

The hydrogen chloride was made by the action of pure sulphuric acid, free from nitrate (diphenylamine reaction), on fused ammonium chloride, free from carbonate and nitrate. The gas was passed through two towers tightly packed with glass wool and was frequently tested for sulphuric acid spray; none was detected.

Pipettes and burettes were standardised by weight.

For experiments in which the concentration was so low that there was no fuming, 400-c.c. glass bottles with ground stoppers and special caps were used. About 80 c.c. each of benzene and distilled water were placed in a bottle and hydrogen chloride was bubbled in for the requisite time. The bottle was then placed in a rocker in a thermostat at 20·00° for 6 hours, the contents were allowed to settle during a further 3 hours, and the two layers were removed by syphons. The aqueous layer was titrated with baryta. The hydrogen chloride in the benzene layer was determined by extracting

FIG. 1A.

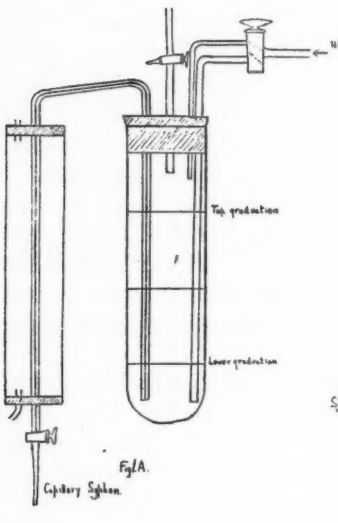
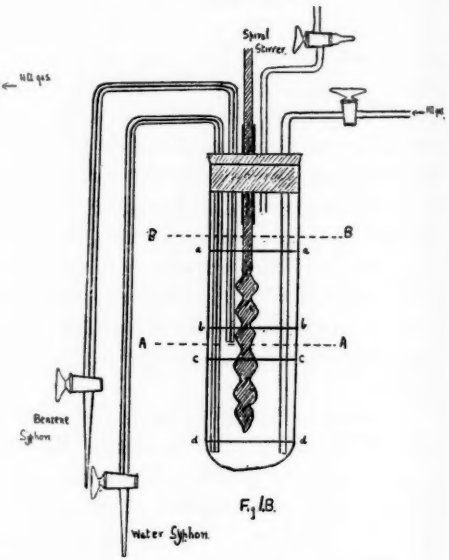



FIG. 1B.




10 c.c. with 50 c.c. of boiled-out water, and estimating the hydrogen-ion concentration of the extract by means of "universal indicator" and suitable standards. The results are given in Table III. They show the order of magnitude only, but it is evident that up to a concentration in the water of about 100 g./litre the amount passing into the benzene is very small indeed. Some of that even will be due to the water dissolved in the benzene, so that the values at these very low concentrations are not suitable for such purposes as the calculation of "activities."

The next determinations made were the solubilities of hydrogen chloride in (1) dry benzene; (2) water; (3) benzene saturated with water before saturation with hydrogen chloride; and (4) benzene saturated with water and hydrogen chloride simultaneously.

For measuring the solubility in dry benzene, the saturator used is shown in Fig. 1A. It was graduated, with all tubes in position, to deliver two amounts of 50 c.c. by means of a capillary syphon. The calibrations were found to be correct at 20°, to within about 0·01 c.c., by weighing water. Two inlet tubes for the hydrogen chloride were provided, one reaching below the lower graduation and the other just entering the vessel so that a stream of gas could be passed over the surface of the liquid when necessary. The gas escaped at atmospheric pressure. The syphon by which the liquid was removed was surrounded by a jacket kept filled with water at 20°. The saturator was placed in a thermostat and filled to just above the top graduation with benzene; and dry hydrogen chloride, after passing through a glass coil immersed in the thermostat, was bubbled through for many hours. The benzene was then run out as far as the top graduation, a stream of gas being passed over the surface all the time. The syphon was thus filled with saturated benzene. 50 C.c. were then run slowly into standard alkali, the jet of the syphon being kept below the surface of the liquid. The excess of alkali was titrated, phenolphthalein being used as indicator, since methyl-red is too soluble in benzene.

The results are summarised in Table I for 20·00°.

TABLE I.

| Expt. | Duration of saturation (hrs.). | Pressure (mm.). | Solubility (g./litre of solution). |
|---|---|---|---|
| 1 | 60 | 760·4 | 16·80 |
| 2 | 60 | 761·0 | 16·76 |
| 3 | 60 | 760·4 | 16·82 |
| 4 | 60 | 762·0 | 16·74 |
| 5 | 60 | 761·4 | 16·79 |
| 6 | 72 | 760·8 | 16·81 |
| 7 | 90 | 759·9 | 16·80 |
| | | Mean at 760 mm. | 16·80 |

For determining the solubility in water at 20·00° (Table II), a smaller saturator delivering 10 c.c. was used, and 24 hours were sufficient for saturation.

TABLE II.

| Expt. | Duration of saturation (hrs.). | Pressure (mm.). | Solubility (g./litre of solution). |
|---|---|---|---|
| 1 | 24 | 760·0 | 718·8 |
| 2 | 24 | 766·1 | 717·9 |
| 3 | 24 | 762·4 | 718·8 |
| 4 | 24 | 762·3 | 718·5 |
| 5 | 36 | 760·1 | 718·8 |
| | | Mean at 760 mm. | 718·8 |

The solubility in benzene previously saturated with water was found to be somewhat higher than in dry benzene: at 20·00° and

atmospheric pressure, the results obtained were 18·28, 18·28, 18·32, 18·32, and 18·32 g. per litre.

This value cannot be used in conjunction with the solubility in water to determine the partition ratio at the saturation point, since when the wet benzene becomes saturated with hydrogen chloride it may take up a further amount of water and consequently still more hydrogen chloride. Accordingly, water was introduced into the saturator so that it covered the end of the long hydrogen chloride inlet tube but did not reach to the bottom of the syphon. The results for the solubility under these conditions were 18·47, 18·50, 18·50, and 18·50 g. HCl per litre.

We thus have at 20·0° and 760 mm.:

| | | |
|---|---|---|
| Solubility of hydrogen chloride in water | 718·8 | g. per litre. |
| Solubility of hydrogen chloride in dry benzene | 16·80 | „ „ |
| Solubility of hydrogen chloride in benzene previously saturated with water | 18·31 | „ „ |
| Solubility of hydrogen chloride in benzene simultaneously saturated with water and hydrogen chloride | 18·50 | „ „ |

For partition experiments at high concentrations the apparatus in Fig. 1 B was used. It consisted of a glass tube with four etched graduations *aa*, *bb*, *cc*, and *dd*. The volume contained between *aa* and *bb* and between *cc* and *dd* was 50 c.c. The apparatus was calibrated with the tubes in position and with the stirrer lowered to the bottom of the vessel. Two syphons were provided; that to take off the top layer extended for 1 cm. below *bb*, while the other, to take off the bottom layer, extended for 1 cm. below *dd*. Both were made of capillary tubing and were lagged with cotton wool. The apparatus was placed in the thermostat, filled to AA with pure water and then to BB with benzene. Hydrogen chloride was passed in for periods varying from 1 to 48 hours, according to the concentration required. The spiral stirrer was very efficient, breaking up the benzene into tiny globules and distributing these throughout the aqueous layer. After the gas had been allowed to pass for the requisite time, it was turned off, and the stirring was continued for another 2 hours. The stirrer was then disconnected and lowered to the bottom, since the apparatus had been calibrated with it in this position. The two layers were allowed to separate. The benzene was then run down to the graduation *aa*, thereby filling the syphon with solution of the same concentration as that in the bulk of the apparatus. This procedure also served to remove the top layer, which might have gained or lost a little hydrogen chloride during the settling. 50 C.c. of the benzene layer were then run out into standard alkali and titrated. The whole procedure was immediately repeated with the aqueous layer.

The results (Table III) are expressed as g./litre, $C_w$ and $C_B$ representing the concentrations in the water and benzene phases, respectively.

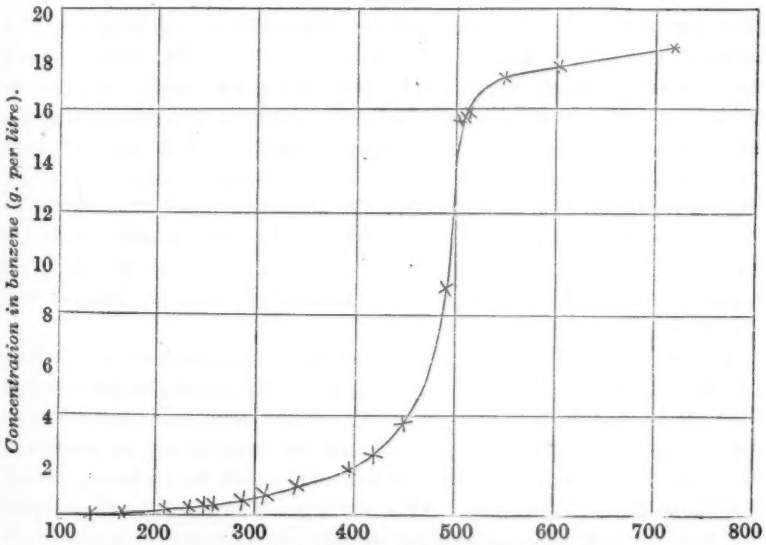
TABLE III.

*Partition of Hydrogen Chloride between Water and Benzene at* 20·0°.

| $C_w$. | $C_B$. | $C_w/C_B$. | $C_w$. | $C_B$. | $C_w/C_B$. | $C_w$. | $C_B$. | $C_w/C_B$. |
|---|---|---|---|---|---|---|---|---|
| 718·8 | 18·50 | 38·85 | 397·3 | 1·85 | 196·0 | 165·9 | 0·100 | 1660 |
| 604·0 | 17·7 | 34·1 | 379·8 | 1·818 | 208·9 | 134·6 | 0·059* | $2·3\times10^3$ |
| 549·3 | 17·4 | 31·6 | 343·3 | 1·264 | 272 | 94·8 | 0·028 | $3·4\times10^3$ |
| 513·3 | 15·99 | 32·1 | 312·0 | 0·929 | 336 | 71·9 | $1·5\times10^{-2}$ | $4·7\times10^3$ |
| 509·0 | 15·71 | 32·4 | 289·3 | 0·706 | 410 | 43·3 | $3·6\times10^{-3}$ | $1·2\times10^4$ |
| 504·6 | 15·62 | 34·2 | 259·0 | 0·532 | 504 | 34·5 | $1·8\times10^{-3}$ | $2\times10^4$ |
| 492·5 | 8·96 | 55·0 | 249·0 | 0·449 | 554 | 19·5 | $2\times10^{-4}$ | $10^5$ |
| 448·5 | 3·72 | 120·7 | 236·1 | 0·382 | 619 | 12·3 | $10^{-4}$ | $1·3\times10^5$ |
| 420·2 | 2·47 | 170·0 | 212·0 | 0·252 | 840 | | | |

* The figures for $C_B$ at and below this point are obtained from colorimetric estimations of hydrogen-ion concentration only; the others are based on volumetric titrations.

FIG. 2.




*Distribution of hydrogen chloride between benzene and water at* 20°.

It is evident from Fig. 2 that, at concentrations between 400 and 550 g./litre in the aqueous layer, there is a rapid passage from the polar to the non-polar form. When this is complete, there is a more or less constant partition ratio as shown by the table. If we regard the concentration in benzene as a measure of the amount of un-ionised hydrogen chloride in the water, then the shape of the curve in Fig. 2 is quite characteristic of an equilibrium between the

ionised and un-ionised forms, the change from one to the other being about half complete at a concentration of about 490 g./litre.

According to uncorrected conductivity and osmotic data, this half-way point would come at much lower concentrations, where the Debye–Hückel theory shows ionisation to be still practically complete. The partition method reveals more nearly the true state of affairs.

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## LXIX.—*Benzyl δ-Chlorobutyl Ether: A New Unsymmetrical Derivative of Tetramethylene Glycol.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

THE preparation of tetramethylene dibromide is no longer a very difficult matter (v. Braun and Lemke, *Ber.*, 1922, **55**, 3526; Marvel and Tanenbaum, *J. Amer. Chem. Soc.*, 1922, **44**, 2645), but unsymmetrical δ-substituted *n*-butyl halides, which have a special importance as synthetic reagents, have been obtained in only two instances and in poor yield. δ-Amyloxy-*n*-butyl bromide was isolated by Hamonet (*Bull. Soc. chim.*, 1905, **33**, 513) and used in a synthesis of pentamethylene dibromide, whilst δ-phenoxybutyl bromide appeared as a by-product in the conversion of δ-phenoxybutyl alcohol into tetramethylene dibromide described by Marvel and Tanenbaum (*loc. cit.*).

Being in need of an unsymmetrical αδ-disubstituted butane of this type, we decided to prepare δ-benzyloxybutyl chloride (benzyl δ-chlorobutyl ether), since the benzyl group has considerable advantages over both the phenyl and the amyl group in respect of the ease with which it is removed and of the fact that a free hydroxyl group is left in the process. This was a point so vital for the purpose we had in view (see succeeding paper) as to render comparatively unimportant our lower yield of δ-benzyloxybutyl alcohol as compared with that of phenoxybutyl alcohol obtained by Marvel and Tanenbaum.

Benzyl β-chloroethyl ether (Bennett, J., 1925, **127**, 1277) showed no tendency to combine with magnesium, an observation which was consistent with the statement by Hamonet (Wurtz, "Dictionnaire de Chimie," **2**, 751) that ethers of the type $RO{\cdot}CH_2{\cdot}CH_2X$ (where X is a halogen) do not yield Grignard reagents. Benzyl iodoethyl ether, however, combined readily with magnesium. The

action of the resulting organo-magnesium compound on β-chloroethyl *p*-toluenesulphonate (compare Gilman and Beaber, *J. Amer. Chem. Soc.*, 1923, **45**, 839), on ethylene oxide and on ethylene chlorohydrin (compare Grignard, *Compt. rend.*, 1903, **136**, 1260; 1905, **141**, 44; Meisenheimer, *Annalen*, 1925, **442**, 180) was studied, but in no case did we isolate enough of the desired product for its identification with certainty, and experiments in this direction were abandoned after we had confirmed the original statements of Grignard.

The method of preparation finally adopted involved the reduction of ethyl γ-benzyloxybutyrate to the δ-benzyloxybutyl alcohol. The required ester was obtained in two ways: (*a*) from ethylene glycol through benzyl chloroethyl ether by the malonic ester method, and (*b*) from trimethylene glycol through its monobenzyl ether, benzyl chloropropyl ether and the corresponding nitrile, $CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$. The practical success of each of these methods depends on the use of thionyl chloride in presence of dimethylaniline to replace the hydroxyl group by chlorine (Darzens, *Compt. rend.*, 1911, **152**, 1314). On the other hand, the corresponding reaction with thionyl bromide has proved less useful, for benzyl γ-hydroxypropyl ether was only partly converted by it into benzyl bromopropyl ether. As the yield was poor and the product impure, a valuable substance for use as an organo-magnesium compound remains inaccessible. With a cheap supply of trimethylene glycol available, the method (*b*) is the more economical, but the yields by the method (*a*) were good.

## Experimental.

*Benzyl γ-Hydroxypropyl Ether.*—The dissolution of sodium metal in hot trimethylene glycol involves considerable charring and the reaction may become uncontrollable if the metal is allowed to melt (compare Noyes, *Amer. Chem. J.*, 1897, **19**, 766). The method recently used (J., 1925, **127**, 1279) with ethylene glycol is inadvisable, since trimethylene glycol forms a stable compound with sodium ethoxide (Parone, *Boll. Chim. Farm.*, 1905, **44**, 481). The required sodium compound was conveniently obtained as follows: To trimethylene glycol (240 g.), covered with dry xylene (200 c.c.) and heated to 130°, sodium (25 g.) was cautiously added in small pieces. The reaction was easily controlled and soon complete. To the mixture, cooled to 120°, benzyl chloride (150 g.) was added in small portions, and the reaction completed by boiling the whole for 15 minutes. After addition of benzene to increase the precipitation of the sodium chloride, the solution was filtered, washed with water and dried, the solvents were evaporated, and the product was

distilled under diminished pressure. The residue of high b. p. containing the dibenzyl ether of the glycol was neglected. *Benzyl γ-hydroxypropyl ether* is an almost colourless oil, b. p. 155°/23 mm., 172°/43 mm., $d_4^{20°}$ (vac.) 1·0474, $n_a^{20°}$ 1·5128, whence $[R_L]_a$ 47·77 (calc., 47·64). It is not miscible with water, but is soluble in alcohol and ether (Found: C, 71·8; H, 8·5. $C_{10}H_{14}O_2$ requires C, 72·2; H, 8·5%). The yield of this monobenzyl ether (128 g.; 70%) was reduced when the temperature of the reaction was higher than 120°. This is to be expected if, as is the case with ethylene glycol (Forcrand, *Compt. rend.*, 1891, **113**, 1048), the heat evolved in the replacement of the second atom of hydrogen by sodium is less than that for the first, since this will cause a redistribution of the equilibrium in the mixture in favour of the disodium compound as the temperature rises. Attempts to prepare a *p*-nitrobenzoate and a phenylurethane derivative of the substance yielded no crystalline products other than *p*-nitrobenzoic acid and diphenylcarbamide.

*Benzyl γ-Chloropropyl Ether.*—Thionyl chloride (120 g.) was added drop by drop to a mixture of benzyl hydroxypropyl ether (160 g.) and dimethylaniline (130 g.) below 60°. After ½ hour, the mixture was poured into dilute hydrochloric acid in excess, and the heavy oil which separated removed with chloroform. The extract was washed with dilute acid to remove dimethylaniline, then with water, and dried over sodium sulphate, the solvent evaporated, and the oil distilled. *Benzyl γ-chloropropyl ether* was at once obtained (153 g.; 83% yield) as a colourless oil, b. p. 129°/16 mm., $d_4^{20°}$ (vac.) 1·0706, $n_a^{20°}$ 1·5102, whence $[R_L]_a$ 50·40 (calc., 50·96) (Found: Cl, 19·4. $C_{10}H_{13}OCl$ requires Cl, 19·2%).

*γ-Benzyloxybutyronitrile*, $CH_2Ph{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CN$.—A solution of benzyl chloropropyl ether (200 g.) and sodium cyanide (85 g.) in water (100 c.c.) and industrial spirit (125 c.c.) was boiled under reflux for 48—60 hours, any alcohol evaporating being replaced from time to time. Benzene was added when the mixture had cooled, and the sodium chloride was then filtered off and the upper layer of benzene was removed, dried over sodium sulphate and distilled in a Widmer vacuum fractionating flask (*Helv. Chim. Acta*, 1924, **7**, 59), a complete separation of the nitrile from any unchanged chloro-compound being thus readily secured; a second distillation gave the analytically pure *γ-benzyloxybutyronitrile*, a colourless oil of faint odour, b. p. 157°/12 mm., 166°/16 mm., $d_4^{20°}$ (vac.) 1·026, $n_a^{20°}$ 1·5005, whence $[R_L]_a$ 50·27 (calc., 50·61) (Found: C, 75·2; H, 7·7. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5%). The yield of nitrile was 100—110 g. (57%) and 25—40 g. of chloropropyl ether were recovered (16%).

*Ethyl γ-Benzyloxybutyrate*, $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et$.—The nitrile (82 g.) was boiled under reflux with absolute ethyl alcohol (95 g.) and concentrated sulphuric acid (45 g.) for 8 hours, half the alcohol removed by distillation, and the residue poured into water. The precipitated oil was separated by means of ether, the extract washed with sodium carbonate solution, dried, and distilled. *Ethyl benzyloxybutyrate* (63—69 g.; 65% yield) was thus obtained as a straw-coloured oil, b. p. 160°/14 mm., $d_4^{20°}$ (vac.) 1·036, $n_a^{20°}$ 1·4930, whence $[R_L]_a$ 62·10 (calc., 61·56) (Found: C, 70·5; H, 8·2. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·2%).

*Alternative Synthesis of Ethyl Benzyloxybutyrate*.—A mixture of ethyl malonate (24 g.), benzyl β-chloroethyl ether (25·6 g.), and sodium ethoxide (from 3·5 g. of sodium) in absolute ethyl alcohol (50 c.c.) was heated in a soda-water bottle at 100° for 6 hours. The alcohol and any unchanged material were removed in a current of steam, the residual oil was separated in ether, and the extract was washed, dried and distilled; *ethyl β-benzyloxyethylmalonate*, $C_7H_7{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CH(CO_2Et)_2$ (17 g.), was then obtained as a colourless liquid of b. p. 213°/22 mm., $d_4^{20°}$ (vac.) 1·0795, $n_a^{20°}$ 1·4908, whence $[R_L]_a$ 78·9 (calc., 77·00) (Found: C, 65·1; H, 7·5. $C_{16}H_{22}O_5$ requires C, 65·3; H, 7·5%).

This ester (40 g.) was carefully added to a solution of potassium hydroxide (22 g.) in ethyl alcohol (100 c.c.), and the mixture boiled for 2 hours. The alcohol was evaporated, and the solution was acidified with dilute sulphuric acid (22 g. of $H_2SO_4$ in 200 c.c. of water) and extracted with ether for 1 day in a continuous extractor. The residue after evaporation of the ether from the dried ethereal solution was heated at 170—180° until evolution of carbon dioxide ceased (2 hours); *γ-benzyloxybutyric acid* (25 g.) was then left as a syrupy liquid. This was at once esterified by boiling it for 7 hours with 10% alcoholic sulphuric acid (250 g.). The ester, isolated in the usual manner, had b. p. 163—166°/18 mm. (23 g.; overall yield from the dicarboxylic ester, 76%).

*Reduction of Ethyl Benzyloxybutyrate*.—The ester was reduced in toluene solution by sodium and ethyl alcohol as described by Marvel and Tanenbaum (*loc. cit.*) in a glass flask with two wide necks down one of which passed the stirrer and the delivery-tube of a dropping-funnel, whilst the other was fitted with the extra-wide metal tube of a long condenser. No difficulty was found in reducing the molten metal to a fine state of division when the stirrer (of the hollow T-piece pattern) was driven directly by an electric motor at high speed. On distillation of the final product, *benzyl δ-hydroxybutyl ether* was obtained (yield 37%) as a colourless oil, b. p. 157°/12 mm., $d_4^{20°}$ (vac.) 1·029, $n_a^{20°}$ 1·5107, whence $[R_L]_a$ 52·46 (calc., 52·24). It is

soluble in alcohol, ether or benzene, but insoluble in water (Found: C, 73·6, 73·5; H, 9·0, 9·1. $C_{11}H_{16}O_2$ requires C, 73·3; H, 9·0%). As was the case with the lower homologue (p. 474), the *p*-nitrobenzoate and phenylurethane of this substance could not be obtained crystalline.

*Benzyl δ-Chlorobutyl Ether.*—Thionyl chloride (6 g.) was gradually added to a well-shaken mixture of benzyl hydroxybutyl ether (9 g.) and dimethylaniline (6 g.), and the product (8 g.; 80% yield) isolated as was the analogous chloropropyl ether (p. 474). *Benzyl chlorobutyl ether* is a pale yellow oil, b. p. 135°/12 mm., $d_4^{20°}$ (vac.) 1·0572, $n_\alpha^{20°}$ 1·5083, whence $[R_L]_\alpha$ 56·10 (calc., 55·56) (Found: Cl, 17·5. $C_{11}H_{15}OCl$ requires Cl, 17·8%).

*Benzyl β-Iodoethyl Ether.*—Benzyl chloroethyl ether (60 g.) was heated for 30 hours in boiling methyl alcohol with sodium iodide (60 g.), the solvent was then evaporated, and the oil was precipitated by water, removed in ether, dried, and distilled under diminished pressure in a Widmer flask. *Benzyl iodoethyl ether* was thus isolated (yield 60%; some chloro-compound was recovered) as a heavy, colourless oil, b. p. 148—149°/14 mm. (Found: I, 48·0. $C_9H_{11}OI$ requires I, 48·4%).

*Experiments with Magnesium β-Benzyloxyethyl Iodide.*—Magnesium dissolved readily in an ethereal solution of benzyl iodoethyl ether. (No reaction was observed with the corresponding chloro-compound.) The resulting Grignard reagent was subjected to the action of β-chloroethyl *p*-toluenesulphonate (1 mol.) either in boiling ether or in boiling benzene, but the ester was largely recovered unchanged together with benzyl ethyl ether. The magnesium benzyloxyethyl iodide was also allowed to react in ethereal solution with ethylene oxide, the solution evaporated, and the residue heated; and, lastly, the Grignard reagent in question was added to a mixture of ethylene chlorohydrin with either magnesium phenyl bromide or magnesium ethyl bromide, and the mixture heated. In none of these experiments was benzyl hydroxybutyl ether identified with certainty among the products. In each case benzyl ethyl ether was obtained in quantity.

THE UNIVERSITY, SHEFFIELD. [*Received, November 30th,* 1926.]

# LXX.—*The Influence of the Sulphur Atom on the Reactivity of Adjacent Atoms or Groups. Part I. A Qualitative Comparison of the Reactivities of Chlorine and Hydroxyl in the α-, β-, γ-, and δ-Positions to a Sulphur Atom.*

By GEORGE MACDONALD BENNETT and ALFRED LOUIS HOCK.

THE study of sulphides substituted in the β- and γ-positions having yielded results of great interest (J., 1925, **127**, 2671), we undertook the preparation of a δ-chlorobutyl sulphide. We did not, in fact, succeed in isolating a free δ-chlorobutyl sulphide, owing to the unexpected reactivity of the δ-hydroxy sulphide and to the tendency of the halogenated sulphide to undergo internal salt-formation with production of the tetramethylene sulphide ring. δ-Halogenated butyl sulphides themselves are apparently capable of only a transitory existence. At the same time, the observations made in the course of these experiments provide ample evidence concerning the reactivity of the hydroxyl group in the δ-position.

The method of synthesis proposed was to convert benzyl δ-chlorobutyl ether (see preceding paper) into δδ′-dibenzyloxydibutyl sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph)_2$, to remove the benzyl groups by means of hydrobromic acid, and subsequently to convert the resulting dihydroxysulphide into the δδ′-dichlorodibutyl sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Cl)_2$. In order to test the applicability of the method, and for purposes of comparison, the analogous reactions were first carried out in the γ-substituted propyl series, namely, the conversion of benzyl γ-chloropropyl ether into the sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2Ph)_2$, and this into the hydroxy-sulphide, $S(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$, and γγ′-dichlorodipropyl sulphide, of which the last two compounds had been previously described (*loc. cit.*). This series of reactions proceeded very smoothly to give an excellent yield of the expected chloropropyl sulphide. δδ′-Dibenzyloxydibutyl sulphide was readily obtained from benzyl chlorobutyl ether and hydrobromic acid removed the benzyl groups quantitatively at laboratory temperature; but, although the reaction had been conducted in a manner precisely similar to that successfully adopted for the conversion of γγ′-dibenzyloxydipropyl sulphide into the hydroxypropyl sulphide, the second product of this fission was not dihydroxydibutyl sulphide. The substance obtained proved to be *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide*,

$$\left[\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{matrix}\!\!>\!S{\cdot}(CH_2)_4{\cdot}OH\right]Br \quad (I)$$

which was characterised as the *picrate*, the *bromoplatinate*, and the

*bromoaurate*. Confirmation of the structure of this substance was furnished by its ready decomposition by heat with liberation of tetrahydrothiophen.

Whereas a tendency in a δ-halogenated sulphide to ring-closure by internal salt-formation might have been anticipated from analogy with corresponding nitrogen compounds, the rapid substitution of bromine for hydroxyl, which must have preceded it,* was entirely unexpected.

*Reactivity of Hydroxyl or Chlorine in the α-, β-, γ-, and δ-Positions Relative to a Sulphur Atom.*—A valid comparison of the reactivities of two compounds can only be made when the reaction involved is the same and proceeds by the same mechanism in the two cases. The reaction of the type $R{\cdot}S{\cdot}(CH_2)_n{\cdot}OH + HCl \rightleftharpoons R{\cdot}S{\cdot}(CH_2)_nCl + H_2O$ which we propose to consider is at least partially reversible, and it seems legitimate, in comparing sulphides substituted in various positions, to make reference to the behaviour of either the hydroxy- or the chloro-sulphide. The high reactivity of both hydroxyl and chlorine in the β-position and the low reactivity of both in the γ-position support this view, which is moreover justifiable from a consideration of the interpretation of this reactivity in terms of electrons (see below). We now include α- and δ-substituted sulphides, therefore, in the comparison, although the evidence refers in the former case only to a chlorosulphide and in the latter to a hydroxysulphide.

It was found by Peters and Walker (*Biochem. J.*, 1923, **17**, 260) that the rate of liberation of acid by hydrolysis in dilute aqueous-alcoholic solution from αα′-dichlorodimethyl sulphide is five times that observed with ββ′-dichlorodiethyl sulphide. Our own experiments, described above, now prove that the hydroxyl group in the δ-position to a sulphur atom has a reactivity with acids of a higher order than that in the γ-position. The reactivities of the hydroxyl group or chlorine atom in these sulphides, with respect to the reactions specified, are therefore related as follows: $\alpha > \beta > \gamma < \delta$.

*Interpretation of this Conclusion with Reference to Electronic Theories of Valency.*—The markedly higher reactivity of αα′-dichlorodimethyl sulphide and ββ′-dichlorodiethyl sulphide as compared with trimethylene and pentamethylene dichlorides respectively shows that the influence of the sulphur atom is the most important factor involved, any mutual effect of the two chlorine atoms being relatively insignificant.

A high reactivity of the hydroxyl group or of the chlorine atom,

* The only alternative supposition would be the self-addition of the δ-hydroxybutyl sulphide to yield the cyclic sulphonium *base*—a reaction for which we can find no analogy in the chemistry of either sulphur or nitrogen.

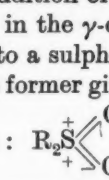
with respect to the reaction studied, must depend on an increased negative charge on the oxygen or chlorine atom. Since the carbon chains in these sulphides are saturated, the possibility of an alternating polarity effect need not be considered. The high reactivity of chlorine in the α- and β-positions may be attributed to a general polar effect of the sulphur atom, which, like bivalent oxygen (compare Rây and Robinson, J., 1925, **127**, 1618), tends to repel electrons and thereby increases the negative charge on the chlorine atoms, the effect being greater in the α- than in the β-position owing to the smaller distance of chlorine from sulphur in the former case. In this process, the sulphur atom becomes positively charged to an extent which is presumably increased by the influence of the chlorine atoms in attracting electrons away from it, the reinforcement of the effect of the sulphur atom under the influence of the chlorine atoms being again greatest in the α-chloro-sulphide :

$$\overleftarrow{\mathrm{Cl}}\cdot\mathrm{CH_2}\cdot\overrightarrow{\mathrm{S}}\cdot\overrightarrow{\mathrm{CH_2}}\cdot\overrightarrow{\mathrm{Cl}} \qquad\qquad \overleftarrow{\mathrm{Cl}}\cdot\mathrm{CH_2}\cdot\overleftarrow{\mathrm{CH_2}}\cdot\overrightarrow{\mathrm{S}}\cdot\overrightarrow{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\overrightarrow{\mathrm{Cl}}$$

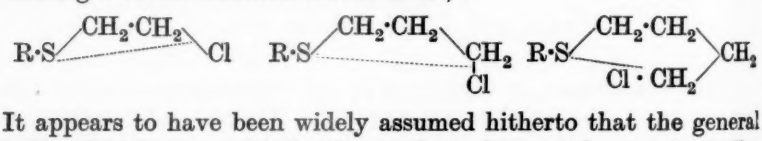
In the case of the γ-chloro-sulphide, these effects will be further diminished owing to the greater distance between sulphur and chlorine. The sulphur atom is here negative (or at least much less positive), and the chlorine atoms are not made reactive :

$$\overleftarrow{\mathrm{Cl}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\overrightarrow{\mathrm{CH_2}}\cdot\overleftarrow{\mathrm{S}}\cdot\overrightarrow{\mathrm{CH_2}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\overrightarrow{\mathrm{Cl}}.$$

These conclusions are supported by the variations in the chemical behaviour of the sulphur atom itself. Whereas methiodides of α- or β-chloro-sulphides are unknown—although evidence that methyl iodide and ββ′-dichlorodiethyl sulphide combine to some extent was obtained by Helfrich and Reid (*J. Amer. Chem. Soc.*, 1920, **42**, 1229)—we were able to isolate a crystalline derivative of the sulphonium methiodide derived from γγ′-dichlorodipropyl sulphide (Bennett and Hock, *loc. cit.*). A similar gradation in properties of the sulphur atom in these compounds is evident in the ease and extent of their oxidation either to a sulphoxide or to a sulphone, for the sulphoxide of αα′-dichlorodimethyl sulphide and both the sulphoxide and the sulphone of ββ′-dichlorodiethyl sulphide have been described, whilst we found it impossible to isolate the sulphoxide of the γ-chloro-sulphide, the sulphone being formed in all cases. In both these respects, therefore, involving addition of methyl iodide or of oxygen, the reactivity of the sulphur atom varies in the order $\alpha<\beta<\gamma$. This conclusion is exactly what would be expected as a consequence of the electronic distribution already discussed. The sulphur atom in the α- and to a less extent in the

β-chloro-sulphide, being already positively charged, will tend to prevent the addition of methyl iodide. The negative nature of the sulphur atom in the γ-chloro-sulphide, on the other hand, explains its oxidation to a sulphone rather than a sulphoxide, since the production of the former gives to the sulphur atom two positive charges instead of one:  .

The high reactivity of the hydroxyl group in the δ-position to the sulphur atom is, however, the most interesting result to be considered, since it furnishes definite evidence that the general polar effect, in this case at least, operates chiefly through space rather than along the chain of carbon atoms. For it is clear that if the effect of the sulphur atom on the chlorine or hydroxyl in the γ-position is only slight, its effect on the δ-hydroxyl group, if transmitted exclusively along the chain, must be negligible. At the same time, the rapid transformation of the corresponding halogenated sulphide into the cyclic sulphonium salt (I) provides experimental proof that a substituent in the δ-position does actually approach close to the sulphur atom in space, and the conclusion appears inevitable that the reactivity of the δ-substituent is due to a direct effect of the sulphur atom on it (or on the electron pair binding it to the terminal carbon atom):



It appears to have been widely assumed hitherto that the general polar effect is transmitted either exclusively, or at least principally, along the chain of atoms. Allan, Oxford, Robinson, and Smith, for instance (J., 1926, 406, footnote), mention "possibly also an electrical effect exercised across the intervening space rather than through the chain." Our observations appear to place this possibility beyond doubt. It is probable that the general polar effect, like the alternating effect, is more readily transmitted by an unsaturated than by a saturated chain, there being more freedom of movement of electrons in the former. The chain is saturated in the case under discussion, where the effect through space has now been demonstrated, but a similar effect transmitted through space may be anticipated also where the chain is unsaturated.

## EXPERIMENTAL.

*γγ'-Dibenzyloxydipropyl Sulphide.*—Benzyl γ-chloropropyl ether (9·2 g.) was heated for 6 hours with a solution of sodium sulphide (15 g. of $Na_2S,9H_2O$) in 50% aqueous alcohol (20 c.c.), the mixture

poured into water, the oil removed in ether, and the solution washed, dried, and evaporated. The pale yellow oil (7·3 g.) left after heating for an hour at 120° under diminished pressure in a current of air was *γγ′-dibenzyloxydipropyl sulphide*, but did not crystallise and was not analysed. This substance reacted readily with fuming hydrobromic acid in the cold. After the mixture had been kept for 24 hours at the ordinary temperature, the acid and the benzyl bromide which had been produced were removed in a current of steam, and all volatile matter was then driven off by heating under diminished pressure. The residue (3·6 g.) was *γγ′*-dihydroxydipropyl sulphide, since the action of thionyl chloride (6·4 g.) and dimethylaniline (6·4 g.) readily converted it into the corresponding chloropropyl sulphide, b. p. 150—160°/35 mm. (2·8 g.; 77% yield from the benzyl chloropropyl ether).

*δδ′-Dibenzyloxydibutyl Sulphide.*—Benzyl δ-chlorobutyl ether (see preceding paper) (9·2 g.) was subjected to the action of aqueous-alcoholic sodium sulphide solution precisely as described above for the corresponding chloropropyl ether, and was thus converted into *δδ′-dibenzyloxydibutyl sulphide* (8 g.), a pale yellow oil which could not be distilled and did not solidify.

*Action of Hydrobromic Acid on δδ′-Dibenzyloxydibutyl Sulphide.*—Dibenzyloxydibutyl sulphide (8 g.) was covered with 48% hydrobromic acid, hydrogen bromide passed into the cooled mixture to saturation, and the whole kept at the ordinary temperature for 24 hours. A current of steam was passed to remove volatile products, and a heavy oil (7·4 g.) was then collected, b. p. 190—205°, *d* 1·46, identified as benzyl bromide (b. p. 198°, $d^{15°}$ 1·43; calculated yield, 7·9 g.). The residual aqueous solution was evaporated several times, and with addition of more water, under diminished pressure in order to remove free acid, and finally dried in a current of air under diminished pressure at 100°. The residue left after these operations had been completed was a viscous material readily soluble in cold water, but insoluble in ether or benzene, and by analogy with the corresponding product derived in a similar way from dibenzyloxydipropyl sulphide it was at first assumed to be dihydroxydibutyl sulphide. Yet the action of phenylcarbimide in benzene and of *p*-nitrobenzoyl chloride at 130° yielded no crystalline derivative, diphenylcarbamide and *p*-nitrobenzoic anhydride (m. p. 181°, not depressed by admixture of an authentic specimen) being produced respectively, whereas the dihydroxydipropyl sulphide reacts readily with phenylcarbimide (compare Bennett and Hock, J., 1925, **127**, 2673) and it is readily converted, when heated at 130° for 1 hour with *p*-nitrobenzoyl chloride (2 mols.), into *di*-p-*nitrobenzoyloxydipropyl sulphide*, pale yellow needles,

m. p. 104—105°, from benzene–light petroleum (Found: N, 6·4. $C_{20}H_{20}O_8N_2S$ requires N, 6·3%). The residue was also subjected to the action of thionyl chloride (2 mols.) in presence of dimethylaniline and alternatively of pyridine (2 mols.), but no insoluble dichloro-compound was obtained. A closer examination of the substance then showed it to be *tetrahydrothiophen-δ-hydroxybutylsulphonium bromide* (I). Attempts to induce crystallisation or to purify it by precipitation of its solution in ethyl alcohol by ether were unsuccessful. The aqueous solution contained ionic bromine in quantity, and when shaken with freshly-precipitated silver oxide yielded a caustic solution which liberated ammonia from ammonium chloride. With aqueous sodium picrate, a *picrate* was produced which solidified in contact with ethyl alcohol and crystallised in yellow needles, m. p. 189—190°. Heated at 250° with nitric acid and silver nitrate in a sealed tube, it yielded no silver bromide. Owing to an unexpected transformation of the sulphonium bromide on keeping for several weeks (see p. 483), no analysis of this picrate could be made.

Precipitation of the aqueous acetone or alcoholic solution of the sulphonium bromide with mercuric bromide under various conditions gave white solids of m. p. 110—135° and 150—200°, which did not seem to be definite chemical individuals and were not further examined. The *bromoplatinate* is a buff, microcrystalline powder insoluble in water and most organic solvents but readily soluble in glycerol-α-dichlorohydrin, and decomposes without melting at 165—170° (Found: Pt, 19·4, 19·2; Br, 49·7. $C_{16}H_{34}O_2Br_6S_2Pt$ requires Pt, 19·6; Br, 48·1%). The *bromoaurate* was precipitated from aqueous solution as a viscous mass which then solidified to a reddish-purple solid; after being washed with water and ether, and dried at the ordinary temperature, it melted with decomposition at 65—70° (Found: Au, 28·9; Br, 48·4. $C_8H_{17}OBr_4SAu$ requires Au, 29·1; Br, 47·3%).

When the dibenzyloxydibutyl sulphide (2 g.) and saturated hydrobromic acid (3·5 g.) were heated together in a sealed tube at 120—150° for 6 hours, the products were identical with those obtained when the reaction occurred at the ordinary temperature. The picrate, m. p. 190°, was readily obtained pure and shown to be identical with the picrate described above, and it was again found to be free from bromine.

*Decomposition of Tetrahydrothiophen-δ-hydroxybutylsulphonium Bromide by Heat.*—When the crude sulphonium bromide was heated, it decomposed readily, the products being almost entirely of a volatile nature. Some two-thirds of the distillate collected during the operation had b. p. 110—135°, and the remainder had b. p.

140—185°. The former fraction, which had an unpleasant odour, was separated from a little water and dried, and was then identified as tetrahydrothiophen (tetramethylene sulphide) by the preparation of its methiodide, m. p. 195—197° (decomp.) (Found: I, 54·4. Calc.: I, 55·1%) (v. Braun and Trümpler, *Ber.*, 1910, **43**, 547, give the b. p. of tetrahydrothiophen as 119° and the m. p. of the methiodide as 185—190°), its mercurichloride, m. p. 125—128° (decomp.) [Grischkevitch-Trochimovski, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 901, gives 124·5—125·5° (decomp.): recrystallisation of this mercurichloride raised the m. p. to 127—133° (decomp.), but the smell of the parent sulphide was evident in the mother-liquor], and the *bromoplatinate*, an orange-red solid darkening at 230° and decomposing at 236—238° (Found: Pt, 28·5; Br, 45·8. $C_8H_{10}Br_4S_2Pt$ requires Pt, 28·2; Br, 46·2%).

*Tetrahydrothiophen-δ-bromobutylsulphonium Bromide.*—It was found that this substance had been unexpectedly produced from a sample of the δ-hydroxybutylsulphonium bromide which, without having been completely freed from hydrobromic acid, had been left for several weeks in a desiccator. When this was converted into its picrate, the oily substance would not crystallise on inoculation with the picrate of m. p. 190°, but it finally solidified at 0° and after eight crystallisations from ethyl alcohol, *tetrahydrothiophen-δ-bromobutylsulphonium picrate* was obtained as bright yellow needles, m. p. 92—96°, quite distinct from the picrate of m. p. 190° described above (Found: C, 36·7; H, 4·3; Br, 16·6. $C_{14}H_{18}O_7N_3BrS$ requires C, 37·2; H, 4·0; Br, 17·7%). This picrate decomposed when kept for a few days at the ordinary temperature (compare the decomposition of dimethyl-β-hydroxyethylsulphonium iodide, Renshaw, Bacon, and Roblyer, *J. Amer. Chem. Soc.*, 1926, **48**, 517). Its production is not easily accounted for in view of the fact that it was not formed in the experiment described above where the reaction was conducted in a sealed tube at 100°. It is conceivable, however, that its isolation in this case may be due to the partial dissociation of the hydroxybutylsulphonium bromide, the conversion of the δ-bromobutyl alcohol liberated into αδ-dibromobutane, and recombination of the latter with the tetrahydrothiophen to yield a bromobutylsulphonium salt.

We wish once more to express our thanks to the West Riding County Council for a scholarship which has enabled one of us (A. L. H.) to take part in the investigation recorded in this and the preceding paper, and to the Chemical Society for a grant which has defrayed some of the expense involved.

THE UNIVERSITY, SHEFFIELD. [*Received, November 30th*, 1926.]

# LXXI.—*The Condensation of Substituted Anilines with* cyclo*Pentanone Cyanohydrin. Derivatives of* 1-*Anilino*cyclo*pentane*-1-*carboxylic Acid.*

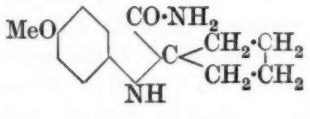
By Stephen Hellicar Oakeshott and Sydney Glenn Preston Plant.

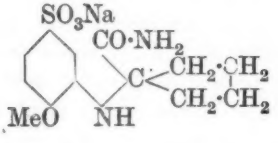
It has already been shown that 1-anilino*cyclo*pentane-1-carboxylic acid and the corresponding 1-*p*-toluidino-compound give carbazole and 3-methylcarbazole, respectively, on fusion with a mixture of potassium hydroxide and sodium ethoxide (Plant and Facer, J., 1925, **127**, 2037; Oakeshott and Plant, J., 1926, 1210). With a view to extend this reaction and establish the structures of some carbazole compounds, the preparation of a number of derivatives of 1-anilino*cyclo*pentane-1-carboxylic acid has been investigated. The general method of procedure has been to prepare the corresponding nitrile by mixing the required amine with *cyclo*pentanone (rather more than 1 mol.) in glacial acetic acid with the subsequent addition of aqueous potassium cyanide (about 1½ mols.) (compare the preparation of 1-anilino-1-cyano*cyclo*hexane, Walther and Hübner, *J. pr. Chem.*, 1916, **93**, 124). The direct hydrolysis of the nitrile to the corresponding acid in several cases was difficult, but an almost quantitative conversion could be obtained if the nitrile was first converted into the amide and subsequently into the acid. It was observed in some instances that the nature and position of the substituent in the aniline molecule considerably retarded the formation of the corresponding nitrile, and a detailed study of this was undertaken. The presence of a methyl or methoxyl group in the benzene ring, whatever its position with respect to the amino-group, did not influence the condensation, the reaction being completed during the course of an hour at room temperature. The nitro-group had the greatest effect, this being most pronounced when the nitro-group was in the ortho-position, and least when it was in the meta-position, to the amino-group. Thus *o*-nitroaniline could not be made to condense at all, even when the mixture was heated in a sealed tube at 100° for 5 days, *p*-nitroaniline reacted during 2 days if the temperature was kept at 40—45°, while the reaction with *m*-nitroaniline took place slowly at room temperature, several hours being required for its completion. The effect of the carboxyl group was similar, but not so pronounced, anthranilic acid requiring a few days at 40—45°, *p*-aminobenzoic acid 24 hours at this temperature, whilst *m*-aminobenzoic acid reacted completely in a few hours at room temperature. The retarding effect of chlorine and bromine was negligible, except when the group was

ortho to the amino-group, in which case several hours were required at room temperature for the completion of the reaction.

The formation of the amide from the corresponding nitrile proceeded smoothly, by keeping in concentrated sulphuric acid solution for 2 days, in all cases except some in which a methoxyl group was present. It was possible to convert 1-p-*anisidino*-1-*cyano*cyclo*pentane* into the *amide* (I), but with the corresponding o-*anisidino*- and m-*anisidino*-compounds sulphonation took place at the same time. From 1-o-*anisidino*-1-*cyano*cyclo*pentane* the sodium salt of a monosulphonic acid was isolated, and, since no apparent sulphonation takes place with the *p*-anisidino-compound or in the absence of the methoxyl group, it seems certain that the sulphonyl group enters the position para to the methoxyl group to give *sodium* 1-o-*anisidino*cyclo*pentane*-1-*carboxyamide*-5′-*sulphonate* (II).

(I.)




(II.)

1-*Veratrylamino*-1-*cyano*cyclo*pentane* and 1-mm′-*dimethoxyanilino*-1-*cyano*cyclo*pentane* were prepared from veratrylamine and 3 : 5-*dimethoxyaniline*, respectively, in order to investigate the possibility of obtaining the corresponding dimethoxy-derivatives of $\psi$-indoxyl-*spirocyclo*pentane (compare Perkin and Plant, J., 1923, **123**, 676) by interaction of the cyano-group and the hydrogen atom in the ortho-position in the benzene nucleus under conditions similar to those used by Hoesch (*Ber.*, 1915, **48**, 1122) for condensing nitriles with certain hydroxybenzene compounds. Several attempts to bring about this reaction in dry ether in the presence of zinc chloride or aluminium chloride and dry hydrogen chloride were unsuccessful, the nitriles being recovered unchanged. The failure of this reaction may be accounted for by the absence of an unmethylated hydroxyl group in the benzene nucleus or by the basic nature of the substance.

Fusion of 1-o-*toluidino*cyclo*pentane*-1-*carboxylic acid* with a mixture of potassium hydroxide and sodium ethoxide has given rise to 1-methylcarbazole, which was identified by comparison with a specimen of 1-methylcarbazole prepared by oxidising 8-methyltetrahydrocarbazole. The fact that this fusion gives rise to 1-methylcarbazole and not to 1 : 8-dimethylcarbazole confirms our previous evidence for the view that the formation of carbazole from 1-anilino-*cyclo*pentane-1-carboxylic acid involves the enlargement of the *cyclo*pentane ring (*loc. cit.*).

## EXPERIMENTAL.

1-o-*Toluidino*cyclo*pentane*-1-*carboxylic Acid.*—*o*-Toluidine (27·5 g.) and *cyclo*pentanone (21 g.) were mixed in glacial acetic acid (200 c.c.) and then treated at room temperature with potassium cyanide (20 g.), dissolved in water (60 c.c.). After a short time, the product separated as an oil which, on stirring, solidified, and, after crystallisation from low-boiling petroleum, 1-o-*toluidino*-1-*cyano*cyclo*pentane* was obtained in good yield as colourless prisms, m. p. 68°. A solution of this in concentrated sulphuric acid was kept for 2 days and poured on to ice, and the liquid made alkaline with ammonia. 1-o-*Toluidino*cyclo*pentane*-1-*carboxyamide*, which was precipitated, separated from petroleum in colourless prisms, m. p. 122°. The amide, on being rubbed with concentrated hydrochloric acid, gave its *hydrochloride*, which was added to an excess of hydrochloric acid and the mixture boiled to dryness. The residue was dissolved in aqueous sodium hydroxide, and the filtered solution treated with an excess of glacial acetic acid. This precipitated 1-o-*toluidino*-cyclo*pentane*-1-*carboxylic acid*, which separated from xylene in colourless needles, m. p. 128° (Found: N, 6·5. $C_{13}H_{17}O_2N$ requires N, 6·4%). The acid was unaltered by heating with an excess of potassium hydroxide up to 300°. From an aqueous solution of the cooled mixture, the substance was recovered by the addition of acetic acid.

1-*Methylcarbazole.*—1-*o*-Toluidino*cyclo*pentane-1-carboxylic acid (16 g.) was mixed with potassium hydroxide (35 g.) and sodium ethoxide (40 g.) and heated from 270° to 320° during ½ hour. After cooling, the pulverised product was treated with water, and the insoluble portion dried and distilled. The colourless distillate was crystallised from petroleum, 1-methylcarbazole separating in colourless plates, m. p. 117° (compare Ullmann, *Annalen*, 1903, **332**, 87). Its picrate separated from hot alcohol in scarlet needles, m. p. 144° (compare Ullmann, *loc. cit.*). The 1-methylcarbazole obtained in this way dissolved in concentrated sulphuric acid to give a pale green solution, the colour of which faded in 30 seconds to straw-yellow. The addition of a drop of concentrated nitric acid to this solution produced an intense green colour.

1-Methylcarbazole was also synthesised in the following way: *o*-Tolylhydrazine (12·2 g.) and *cyclo*hexanone (9·8 g.) were heated together on the steam-bath for a short time, and, on cooling, *cyclo*-hexanone-*o*-tolylhydrazone was obtained as a solid mass. The crude hydrazone was heated to boiling with dilute sulphuric acid for a few minutes; the 8-methyltetrahydrocarbazole which separated crystallised from aqueous alcohol in colourless plates, m. p. 98°. 8-Methyltetrahydrocarbazole has previously been prepared by the

interaction of chloro*cyclo*hexanone and *o*-toluidine, and found to melt at 98° (D.R.-P. 374,098). A solution of 8-methyltetrahydrocarbazole (6 g.) and sulphur (2·1 g.) in pure quinoline (20 c.c.) was boiled for 20 minutes and then poured into a mixture of dilute hydrochloric acid and ice. The oil which separated gradually solidified, and was collected, dried, and distilled with an equal volume of iron powder. The distillate, m. p. 110°, was converted into its picrate, which separated from hot alcohol in scarlet needles, m. p. 144°. On warming the picrate with aqueous sodium hydroxide, 1-methylcarbazole, m. p. 117°, was obtained. The fact that this product was identical with that obtained from 1-*o*-toluidino*cyclo*pentane-1-carboxylic acid was established by a mixed m. p. determination, by the colour changes in concentrated sulphuric acid solution, and by the melting points of their picrates.

1-m-*Toluidino*cyclo*pentane*-1-*carboxylic Acid*.—*m*-Toluidine (10 c.c.) and *cyclo*pentanone (8·5 c.c.), dissolved in glacial acetic acid (50 c.c.), were treated at room temperature with potassium cyanide (7 g.), in a little water; an oily product gradually separated. After 2 hours, the mixture was poured into an excess of water, the oily nitrile gradually solidified, and 1-m-*toluidino*-1-*cyano*cyclo*pentane* was obtained as a colourless solid, m. p. 53°, on rubbing with petroleum. This nitrile was hydrolysed in the same way as the corresponding *o*-toluidino-compound and the 1-m-*toluidino*cyclo*pentane*-1-*carboxyamide* obtained separated from aqueous alcohol in colourless prisms, m. p. 145°. The clear solution of the amide in concentrated hydrochloric acid was boiled under reflux for 1 hour and evaporated to dryness, the residue was dissolved in aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. The product was crystallised from aqueous alcohol and 1-m-*toluidino*cyclo*pentane*-1-*carboxylic acid* obtained in colourless needles, m. p. 123—124° (Found: N, 6·5. $C_{13}H_{17}O_2N$ requires N, 6·4%).

*Condensation of the Methoxyanilines with* cyclo*Pentanone Cyanohydrin*.

1-o-*Anisidino*-1-*cyano*cyclo*pentane*.—The reaction mixture was kept at room temperature for 2 hours and then poured into water, the oily product was extracted with ether, and the ethereal solution shaken twice with water and then with dilute aqueous sodium carbonate. On drying the solution with calcium chloride and removing the ether, 1-o-*anisidino*-1-*cyano*cyclo*pentane* remained as a brown syrup. Its solution in concentrated sulphuric acid was kept for 2 days and then poured into ice-water. Calcium carbonate was added to the hot solution until effervescence ceased, and, after filtering, it was treated with a slight excess of sodium carbonate to precipitate the

calcium, again filtered, and evaporated to dryness. The residue was extracted with hot alcohol, acetone was added to the clear alcoholic solution, and, on standing, *sodium* 1-o-*anisidino*cyclo*pentane*-1-*carboxyamide*-5′-*sulphonate* separated in colourless prisms (Found: S, 9·6. $C_{13}H_{17}O_5N_2SNa$ requires S, 9·5%). This sodium salt is very soluble in water.

1-m-*Anisidino*-1-*cyano*cyclo*pentane*.—From the reaction mixture at room temperature, the oily product gradually separated during 1 hour. After dilution with water, the oil solidified on being rubbed with alcohol, and, on crystallisation from this solvent, 1-m-*anisidino*-1-*cyano*cyclo*pentane* separated in colourless prisms, m. p. 132°. The solution of this product in concentrated sulphuric acid became dark green, and was poured into ice-water after 2 days; from the intense purple solution produced, nothing separated on addition of ammonia.

1-p-*Anisidino*cyclo*pentane*-1-*carboxylic Acid*.—The reaction mixture was treated as described for *o*-anisidine, 1-p-*anisidino*-1-*cyano*cyclo*pentane* being obtained as a brown syrup. By treatment with concentrated sulphuric acid for 2 days, pouring into ice-water, making alkaline with ammonia, and crystallising the product from benzene–petroleum, 1-p-*anisidino*cyclo*pentane*-1-*carboxyamide* was obtained in almost colourless prisms, m. p. 81—82°. The amide was hydrolysed by boiling its clear solution in concentrated hydrochloric acid for ½ hour; this was then evaporated to dryness, the residue dissolved in dilute aqueous sodium hydroxide, and the filtered solution acidified with acetic acid. 1-p-*Anisidino*cyclo*pentane*-1-*carboxylic acid* separates from alcohol in colourless prisms, m. p. 160° (Found: N, 6·0. $C_{13}H_{17}O_3N$ requires N, 5·9%).

1-*Veratrylamino*-1-*cyano*cyclo*pentane*.—From the reaction mixture, after a short time, the addition of ammonia precipitated 1-*veratrylamino*-1-*cyano*cyclo*pentane*, which separated from benzene–petroleum in colourless plates, m. p. 98° (Found: N, 11·3. $C_{14}H_{18}O_2N_2$ requires N, 11·4%). When this nitrile dissolves in concentrated sulphuric acid, sulphonation apparently takes place, since dilution of the solution after 2 days and treatment with ammonia gives no precipitate.

1-mm′-*Dimethoxyanilino*-1-*cyano*cyclo*pentane*.—3 : 5-Dimethoxynitrobenzene was obtained from trinitrobenzene by the steps described by Vermeulen (*Rec. trav. chim.*, 1906, **25**, 26), although the following conditions for the methylation of 5-nitro-3-hydroxyanisole were found to be more satisfactory than those given. The anisole (8 g.), methyl sulphate (7·4 g.), and potassium carbonate (8 g.) were mixed in toluene (200 c.c.) and boiled for 4 hours. The toluene was removed in steam and, on cooling the residue, 3 : 5-dimethoxynitro-

benzene solidified; after recrystallisation from ethyl acetate, it melted at 89°.

The most convenient conditions for reducing this compound are similar to those used by Hope and Robinson (J., 1911, **99**, 1159) for reducing anhydrocotarnine-5-nitrophthalide. 3 : 5-Dimethoxynitrobenzene (10 g.) was dissolved in a mixture of glacial acetic acid (100 c.c.) and water (100 c.c.), tin (1 g.) was added, followed by a solution of stannous chloride (6 g.) in hydrochloric acid (60 c.c.), the mixture being then stirred vigorously and maintained at 40° for a few hours. After being made alkaline with sodium hydroxide, the product was extracted with ether and the ethereal solution was shaken with water and dried over sodium sulphate. The ether was removed, and 3 : 5-*dimethoxyaniline* (3·5 g.) obtained on distillation, b. p. 178°/20 mm. On treating the amine with an excess of acetic anhydride and then mixing the product with benzene–petroleum, a solid was obtained. This was crystallised from water, 3 : 5-*dimethoxyacetanilide* separating in colourless needles, m. p. 157° (Found : N, 7·3. $C_{10}H_{13}O_3N$ requires N, 7·2%).

A mixture of 3 : 5-dimethoxyaniline (5 g.), *cyclo*pentanone (3 c.c.), and concentrated aqueous potassium cyanide (3 g.) in glacial acetic acid (30 c.c.), after standing at room temperature for a short time, was partly neutralised with ammonia. The dark-coloured oil that separated was extracted with ether, the extract was twice shaken with water and dried over sodium sulphate, and the solvent removed. The dark oily residue was obtained in colourless plates after successive treatments with low-boiling petroleum. 1-mm'-*Dimethoxyanilino*-1-*cyano*cyclo*pentane* melts at 150° (Found : N, 11·1. $C_{14}H_{18}O_2N_2$ requires N, 11·4%).

*Condensation of the Chloroanilines with* cyclo*Pentanone Cyanohydrin.*

1-o-*Chloroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was left at room temperature for 12 hours, and then poured into dilute hydrochloric acid to remove any unchanged *o*-chloroaniline, but the oily product which separated did not solidify after several hours. The mixture was shaken with ether and the ethereal solution was washed with water and dilute aqueous sodium carbonate and dried over calcium chloride. After removal of the ether, 1-o-*chloroanilino*-1-*cyano*cyclo*pentane* remained as a yellow oil. This was dissolved in concentrated sulphuric acid and the solution was kept for 2 days and poured on to ice. Dilution with water, without the addition of ammonia, caused the separation of the product as a sticky solid, which hardened on being rubbed with petroleum. After crystallisation from petroleum, 1-o-*chloroanilino*-cyclo*pentane*-1-*carboxyamide* was obtained in colourless prisms,

m. p. 113° (Found: N, 11·6. $C_{12}H_{15}ON_2Cl$ requires N, 11·7%). The amide was hydrolysed by boiling its solution in concentrated hydrochloric acid for an hour, and the product isolated by the method employed in the previous cases. After crystallisation from aqueous alcohol, 1-o-*chloroanilino*cyclo*pentane*-1-*carboxylic acid* was obtained in colourless needles, m. p. 145° (Found: N, 5·8. $C_{12}H_{14}O_2NCl$ requires N, 5·8%).

1-m-*Chloroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept for 1 hour at room temperature and then poured into water; the product separated as an oil which slowly solidified on stirring. After crystallisation from low-boiling petroleum, 1-m-*chloroanilino*-1-*cyano*cyclo*pentane* was obtained in colourless prisms, m. p. 47°. Its solution in concentrated sulphuric acid, after 2 days, was poured on to ice, and the product isolated by making it alkaline with ammonia; the 1-m-*chloroanilino*cyclo*pentane*-1-*carboxyamide* obtained crystallised from aqueous alcohol in colourless prisms, m. p. 118°. A solution of this in concentrated hydrochloric acid was boiled for ½ hour, the product isolated as before, and, after crystallisation from aqueous alcohol, 1-m-*chloroanilino*cyclo*pentane*-1-*carboxylic acid* was obtained in colourless prisms, m. p. 112° (Found: N, 5·8. $C_{12}H_{14}O_2NCl$ requires N, 5·8%).

1-p-*Chloroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was treated exactly as described for *m*-chloroaniline, and the condensation was complete after 15 minutes. From aqueous alcohol, 1-p-*chloroanilino*-1-*cyano*cyclo*pentane* separated in long, colourless prisms, m. p. 73°. The hydrolysis of this nitrile proceeded exactly as with the *m*-chloroanilino-compound; the 1-p-*chloroanilino*cyclo*pentane*-1-*carboxyamide* obtained crystallised from aqueous alcohol in colourless needles, m. p. 132°. 1-p-*Chloroanilino*-cyclo*pentane*-1-*carboxylic acid* crystallised from benzene in colourless prisms, m. p. 144° (Found: N, 5·5. $C_{12}H_{14}O_2NCl$ requires N, 5·8%).

*Condensation of the Bromoanilines with* cyclo*Pentanone Cyanohydrin.*

1-o-*Bromoanilino*cyclo*pentane*-1-*carboxylic Acid.*—The preparation of this acid followed exactly the same course as that described for the *o*-chloroanilino-derivative. 1-o-*Bromoanilino*-1-*cyano*-cyclo*pentane* was obtained as a yellowish-brown oil, but its complete formation required about 24 hours at room temperature. 1-o-*Bromoanilino*cyclo*pentane*-1-*carboxyamide* separated from petroleum in colourless prisms, m. p. 128°, and 1-o-*bromoanilino*cyclo*pentane*-1-*carboxylic acid* from aqueous alcohol in colourless prisms, m. p. 140° (Found: N, 4·9. $C_{12}H_{14}O_2NBr$ requires N, 4·9%).

1-m-*Bromoanilino*cyclo*pentane*-1-*carboxylic Acid.*—The formation

of 1-m-*bromoanilino*-1-*cyano*cyclo*pentane* took place under the conditions described for the corresponding *m*-chloroanilino-compound, but the product separated as an oil and, after extraction with ether, it was ultimately obtained as a yellowish-brown syrup. 1-m-*Bromoanilino*cyclo*pentane*-1-*carboxyamide* separated from aqueous alcohol in colourless plates, m. p. 126°, and 1-m-*bromoanilino*cyclo*pentane*-1-*carboxylic acid* in colourless needles, m. p. 130° (Found : N, 4·9. $C_{12}H_{14}O_2NBr$ requires N, 4·9%).

1-p-*Bromoanilino*cyclo*pentane*-1-*carboxylic Acid.*—The formation of this compound followed the course described for the *p*-chloroanilino-derivative. 1-p-*Bromoanilino*-1-*cyano*cyclo*pentane* separated from petroleum in colourless plates, m. p. 69°, 1-p-*bromoanilino*cyclo*pentane*-1-*carboxyamide* from aqueous alcohol in colourless plates, m. p. 145°, and 1-p-*bromoanilino*cyclo*pentane*-1-*carboxylic acid* from aqueous alcohol in colourless prisms, m. p. 130° (Found : N, 5·2. $C_{12}H_{14}O_2NBr$ requires N, 4·9%).

*Condensation of the Nitroanilines with* cyclo*Pentanone Cyanohydrin.*

1-m-*Nitroanilino*cyclo*pentane*-1-*carboxylic Acid.*—The appropriate mixture was kept at room temperature, the course of the reaction being followed by taking advantage of the fact that *m*-nitroaniline dissolves in dilute hydrochloric acid, whilst the condensation product remains undissolved. On pouring the product into water after 1 hour, it was found that about 80% of the mixture was unchanged *m*-nitroaniline; but after 18 hours the reaction had proceeded practically to completion. 1-m-*Nitroanilino*-1-*cyano*cyclo*pentane* separates from aqueous alcohol in yellow prisms, m. p. 95° (Found : N, 18·0. $C_{12}H_{13}O_2N_3$ requires N, 18·2%). The hydrolysis of this nitrile was carried out in the usual way, and the 1-m-*nitroanilino*-cyclo*pentane*-1-*carboxyamide* obtained separated from aqueous alcohol in orange prisms, m. p. 144° (Found : N, 16·8. $C_{12}H_{15}O_3N_3$ requires N, 16·9%). 1-m-*Nitroanilino*cyclo*pentane*-1-*carboxylic acid* was obtained, after crystallisation from aqueous alcohol, in long, yellow prisms, m. p. 137° (Found : N, 11·4. $C_{12}H_{14}O_4N_2$ requires N, 11·2%).

1-p-*Nitroanilino*cyclo*pentane*-1-*carboxylic Acid.*—As in the case of the *m*-nitroanilino-derivative, the course of the condensation may be followed easily, since the product is insoluble in dilute hydrochloric acid, in which *p*-nitroaniline dissolves. After standing at room temperature for 15 hours, the mixture had undergone very little change, the product being almost entirely soluble in dilute hydrochloric acid. When the reaction mixture was kept in a water-bath at 40—45°, 1-p-*nitroanilino*-1-*cyano*cyclo*pentane* gradually separated in yellow plates during 2 days. A further

quantity of the nitrile was obtained by diluting the mother-liquor with water and crystallising the product from glacial acetic acid. The nitrile separated from this solvent in yellow plates, m. p. 165° (Found: N, 18·2. $C_{12}H_{13}O_2N_3$ requires N, 18·2%). 1-p-*Nitroanilino*cyclo*pentane*-1-*carboxyamide* was obtained by pouring a solution of this nitrile in concentrated sulphuric acid into water after 2 days, without making it alkaline, and separated from alcohol in yellow plates, m. p. 231°. 1-p-*Nitroanilino*cyclo*pentane*-1-*carboxylic acid*, obtained in the usual way, separated from aqueous alcohol in yellow plates, m. p. 187° (Found: N, 11·2. $C_{12}H_{14}O_4N_2$ requires N, 11·2%).

*Condensation of the Aminobenzoic Acids with* cyclo*Pentanone Cyanohydrin.*

*The Amide of* 1-o-*Carboxyanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept for 5 days at 40—45°, and poured into water, and the solid product crystallised from benzene–petroleum, from which 1-o-*carboxyanilino*-1-*cyano*cyclo*pentane* separated in colourless needles, m. p. 122°. Its solution in concentrated sulphuric acid, after being kept for 2 days and then poured into much ice-water, yielded the *amide* of 1-o-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid*, which separated from alcohol in colourless prisms, m. p. 225° (after prolonged drying). An attempt to hydrolyse this amide to the corresponding acid by boiling with concentrated hydrochloric acid for 1 hour and isolating the product in the usual way yielded 1-anilino*cyclo*pentane-1-carboxylic acid, m. p. 160—161° (compare Plant and Facer, *loc. cit.*). The identity of this acid was established by analysis (Found: N, 7·0. Calc.: N, 6·8%) and by a mixed m. p. determination. Other attempts to obtain 1-*o*-carboxyanilino*cyclo*pentane-1-carboxylic acid have so far been unsuccessful.

*The Amide of* 1-m-*Carboxyanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept for 4 hours at room temperature, and the product was isolated by pouring the mixture into water, *m*-aminobenzoic acid being soluble in dilute acetic acid. After crystallisation from toluene, 1-m-*carboxyanilino*-1-*cyano*cyclo*pentane* was obtained in colourless needles, m. p. 153°. The solution of the nitrile in concentrated sulphuric acid was kept for 2 days and poured into ice-water, and the mixture was made alkaline with ammonia and then acidified with acetic acid; the *amide* of 1-m-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid* that separated crystallised from water in colourless prisms, m. p. 215° (Found: N, 11·2. $C_{13}H_{16}O_3N_2$ requires N, 11·3%).

When the amide (20 g.) was heated with a mixture of potassium

hydroxide (36 g.) and sodium ethoxide (40 g.) at 270—320° for ½ hour and the product, after cooling, was treated with water, a small quantity of carbazole remained. This was distilled and subsequently crystallised from toluene and was then identified by a mixed m. p. determination and by conversion into its picrate, m. p. 186°.

1-p-*Carboxyanilino*cyclo*pentane*-1-*carboxylic Acid.*—The reaction mixture was kept at 40°, and, during the course of 24 hours, colourless prisms separated. After recrystallisation from glacial acetic acid, 1-p-*carboxyanilino*-1-*cyano*cyclo*pentane* was obtained in colourless prisms, m. p. 189—190°. Hydrolysis was carried out as described for the *m*-carboxyanilino-derivative and, on crystallisation from alcohol, the *amide* of 1-p-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid* separated in colourless prisms, m. p. 272°. The formation of the acid proceeded in the usual way and 1-p-*carboxyanilino*cyclo*pentane*-1-*carboxylic acid* was obtained, after crystallisation from aqueous alcohol, in colourless prisms, m. p. 225° (decomp.) (Found : N, 5·6. $C_{13}H_{15}O_4N$ requires N, 5·6%).

The authors wish to express their thanks to Mr. F. C. Hall for carrying out the analyses given in this paper.

THE DYSON PERRINS LABORATORY,
OXFORD. [*Received, December* 21*st*, 1926.]

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## LXXII.—*Pseudo-ternary Systems containing Sulphur. Part II. The System Sulphur–Benzoic Acid.*

By DALZIEL LLEWELLYN HAMMICK and WINSTON E. HOLT.

KRUYT (*Z. physikal. Chem.*, 1909, **67**, 330) observed that when mixtures of sulphur and benzoic acid are heated slowly, a cloud (new liquid phase) appears in the sulphur-rich layer in the neighbourhood of 170° and disappears on still further raising the temperature. This behaviour is what would be expected if the solubility curve for liquid sulphur in liquid benzoic acid became retrograde in the neighbourhood of 170° and at higher temperatures resumed its original direction, *i.e.*, if the miscibility curve for liquid sulphur and benzoic acid were of the Type $\eta$ predicted by Kruyt as one of the possible types for pseudo-ternary systems containing sulphur (compare *ibid.*, **65**, 486). Kruyt, however, rejects this explanation on the grounds that according to his experiments the solubility of benzoic acid in liquid sulphur increases slightly with temperature in the region where the clouding effect occurs. Further, he claims that at about 170° the solubility of benzoic acid increases from

2·2% when the two phases are left in contact for a few minutes to 2·8% when they remain together for 5—10 hours. He concludes that in the neighbourhood of 170° three liquid layers can coexist, *viz.*, a solution of sulphur in benzoic acid, a solution of benzoic acid in a liquid sulphur that is mainly $S_\lambda$, and a second solution of benzoic acid in a liquid sulphur that is mainly $S_\mu$.

We have determined equilibria in the system sulphur–benzoic acid by the synthetic method used in our previous investigations on sulphur systems (J., 1926, 1995). Weighed quantities of pure sulphur and benzoic acid (m. p. 121·7°) were sealed in bulb tubes and the necks drawn out to long spindles so that the melted contents could be well mixed by rotating the spindles. Equilibrium temperatures were determined by observing the formation and disappearance, in a regulated thermostat, of the cloud of droplets constituting a second liquid phase. The sulphur-rich phases at lower temperatures contain quantities of benzoic acid of the order of 2%, and, as will be seen from Fig. 1, their composition varies with temperature in a complicated way within a very small range of concentrations. Consequently the mixtures had to be made up with the greatest care. The benzoic acid was introduced into the bulbs first, so that any particles adhering to the walls would be swept in by the large excess of sulphur that was introduced next. The loss in weight that occurred on sealing the bulbs was found to be practically constant at 0·001 g. The contents of the bulbs weighed from 4 to 7 g.

The results obtained are given in Table I; $T_1$ denotes the temperatures at which heterogeneous liquid mixtures of sulphur and benzoic acid first become homogeneous. On raising the temperature to $T_2$, the mixture again becomes heterogeneous; at still higher temperatures, it becomes dark and viscous and finally clears again at temperature $T_3$. The accuracy of temperatures $T_1$ and $T_2$ is about $\pm 1°$; the final clearing temperatures, $T_3$, are much more difficult to observe, but are probably correct to $\pm 2°$. All the values of $T$ quoted are means of several observations made with rising and falling temperatures.

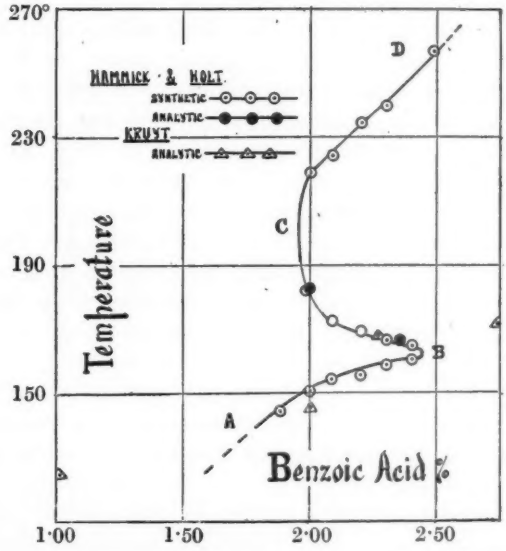
TABLE I.

| Benzoic acid (%) ... | 1·89 | 2·00 | 2·09 | 2·20 | 2·30 | 2·40 | 2·49 |
|---|---|---|---|---|---|---|---|
| $T_1$ ..... | 145° | 151° | 154·5° | 156° | 159·5° | 161·5° | — |
| $T_2$ ..... | — | 183 | 173 | 170 | 167·3 | 165 | — |
| $T_3$ ..... | — | 219 | 225 | 235 | — | 242 | 257·5° |

The above results are plotted in Fig. 1, and it will at once be seen that the diagram gives an explanation of the clouding phenomena observed by Kruyt. Most of his mixtures contained considerable percentages of benzoic acid, and hence, at all temperatures

below the critical solution temperature, he had two liquid layers present. On heating such a mixture, separation of the benzoic-acid-rich phase in the sulphur layer will take place directly the point of inflexion B in Fig. 1 is passed. Owing to the viscosity of the sulphur-rich layer, the separated droplets will not at once coalesce with the benzoic acid layer, but will finally disappear at higher temperatures at some point along the curve CD. Any mixture of sulphur and benzoic acid on cooling from high temperatures will show a clouding effect directly the conditions represented by the curve CD or its prolongation are reached. Between 165° and 175° reabsorption of part or all of the cloud of droplets will

FIG. 1.




occur. When mixtures in which the amounts of benzoic acid lie between 2·0% and 2·4% are used, the above phenomena are more clearly defined and more readily controlled. For instance, a mixture containing 2·30% of benzoic acid is homogeneous at 250°; on cooling, turbidity occurs at about 240° and persists until 167° is reached. The mixture becomes homogeneous again whilst the temperature drops to 159°. The heterogeneous region is now re-entered and the liquid clouds. In short, the sulphur-rich side of the diagram for the system is of the type predicted by Kruyt (*loc. cit.*) as possible in pseudo-ternary sulphur systems, and it is not necessary, in order to account for the clouding phenomena, to suppose that three liquid layers coexist in equilibrium in the neighbourhood of 170°.

There remains, however, the question of the increase in solubility of benzoic acid in liquid sulphur indicated by Kruyt's experiments between 170° and 185° in direct contradiction to our results obtained by the synthetic method. We have therefore made direct analyses of the sulphur layers at 169° and 183°. Mixtures containing roughly equal quantities of sulphur and benzoic acid and weighing 7—8 g. were enclosed in sealed tubes for 4, 8, and 12 hours, respectively, in the vapour of a specimen of phenetole of b. p. 169°. The tubes were rapidly cooled and allowed to stand over-night. They were then opened and about 1 g. of the solid sulphur layer removed. This was dissolved in carbon disulphide and titrated with $N/100$-sodium hydroxide after the addition of alcohol. The percentages of benzoic acid found in the sulphur layer were 2·25, 2·35, and 2·30. Similarly, a mixture kept in the vapour of boiling aniline (183°) for 8 hours gave a sulphur layer containing 2·04% of benzoic acid. These two solubility values are shown on the diagram as large black points and are seen to agree excellently with the results obtained by the synthetic method. Kruyt's value of 2·2% at 169—170° for a mixture heated for a short time agrees well enough with our result; we are, however, unable to confirm the increase in solubility which he found when the heating was prolonged. Furthermore, we find by both the synthetic and the analytic method that the solubility of benzoic acid in sulphur decreases from 169° to 183° (2·30% to 2·04%), whereas Kruyt finds 5·8% at 185° (*loc. cit.*, p. 333).

The discrepancy is probably due to the fact that Kruyt's mixtures were heated in contact with the air, whereas ours were enclosed in sealed tubes. Liquid sulphur can readily be shown to undergo considerable oxidation in the air at the temperatures employed, and the presence of sulphur oxides in the sulphur layer would obviously account for the high values for solubilities deduced from the alkali titre of such a layer. In order to test this view, we heated a mixture in an unsealed tube at the temperature of boiling phenetole (169°) for 10 hours; on analysis the sulphur layer was found to have an apparent content of 2·62% of benzoic acid and gave a positive test for the presence of sulphuric acid with barium chloride.

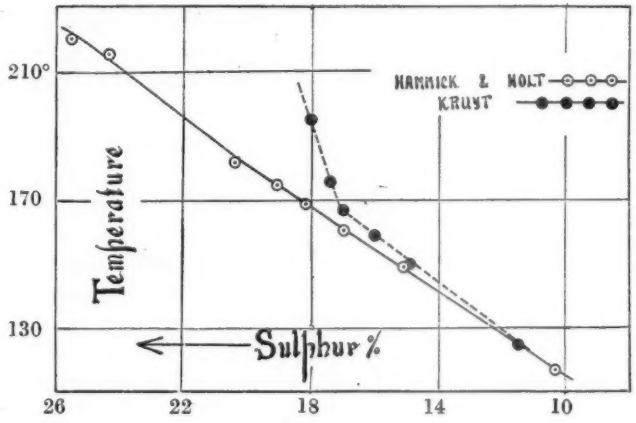
It thus seems to be established that on the sulphur side of the diagram the equilibrium curve is of Kruyt's Type $\eta$; our experiments, however, give no indication of a corresponding inflexion on the benzoic acid side. Our equilibrium temperatures and compositions are given in Table II and are plotted, together with Kruyt's data, in Fig. 2. It will be seen that again we do not agree with Kruyt, whose figures indicate a break in the curve at about 170°.

TABLE II.

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Sulphur (%) | 10·35 | 15·1 | 16·9 | 18·2 | 19·25 | 20·4 | 24·3 | 25·5 |
| Temp. ..... | 117° | 149·5° | 160·5° | 168·5° | 175° | 182° | 215° | 220° |

These equilibria were determined as described above for the sulphur side of the system. The temperatures at which the clouds of second liquid phase separated on slow cooling were sharp, reproducible to within 1°, and remained unchanged on keeping the bulbs for several days. Owing, however, to the rapidity with which the droplets coagulated into large drops, it was not possible to obtain equilibrium temperatures by noticing temperatures at which the droplets disappeared.

FIG. 2.




The benzoic acid side of the system thus appears to be simple. The absence of the clouding and clearing phenomena found on the other side makes it practically certain that the minute region of retrograde solubility found there has no counterpart on the benzoic acid side.

*Summary and Conclusion.*

The diagrammatic representation of the equilibria in the system sulphur–benzoic acid is, on the sulphur side, of Kruyt's Type $\eta$. On the benzoic acid side, it is of the type ordinarily found for two partly miscible liquids. The facts embodied in the whole phase-diagram give an adequate explanation of the clouding phenomena noticed by Kruyt, without the necessity for his conclusion that in the neighbourhood of 170° three liquid layers can coexist.

THE DYSON PERRINS LABORATORY,
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# LXXIII.—*The Effect of Pressure on the Limits for the Propagation of Flame in Ether–Air.*

By Albert Greville White.

In a sufficiently large vessel a wide range of ether–air mixtures can propagate flame upwards or horizontally. Each of these ranges actually consists of two overlapping ranges which differ considerably in character and can be separated under appropriate conditions. Thus the addition of the requisite quantity of acetone to ether–air can give mixtures having two ranges that propagate flame separated

Fig. 1.

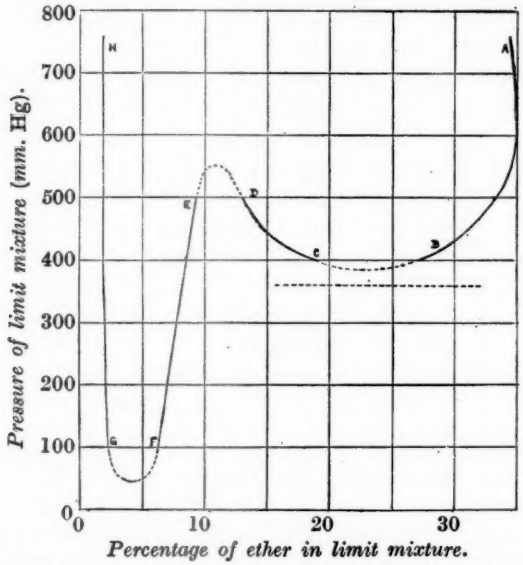


*Figure showing the ranges of ether–air mixtures that can propagate flame horizontally at various pressures.*

by a range that will not (White, J., 1922, **121**, 2561). A similar pair of ranges is given by ether–air alone for horizontal propagation in a narrow tube (2·5 cm. diam.), and within each range the speed of flame increases to a maximum and then decreases as the ether concentration of the mixture is increased (*idem*, *ibid.*, p. 1244).

The results of an examination of the effect of pressure on the limits for the horizontal propagation of flame in ether–air are shown graphically in Fig. 1, and clearly demonstrate the existence of two entirely different propagation ranges. They also provide an explanation of results obtained during similar experiments by

White and Price (J., 1919, **115**, 1462), when the means of ignition adopted was such that the cool-flame range could normally only be obtained as an extension of the ordinary range.

The first notable effect of reduction of pressure is the separation into two ranges, of which the one containing more ether, the cool-flame range ABCD, diminishes rapidly and disappears entirely before the pressure has been reduced to 360 mm. The lower limit changes little until the pressure is 300 mm., but the upper limit of the "ordinary" range EFGH decreases fairly uniformly from 500 mm. to 90 mm. pressure.

## Experimental.

The limits were all determined in cylindrical glass tubes 1·5 m. long and 5·1 cm. in diameter, but their *absolute* values would certainly be altered somewhat by any serious change in the diameter of the tube. The mixture for test was made up in the limit tube by introducing a weighed quantity of ether into the evacuated tube. All mixtures were made up and mixed at the ordinary pressure, and brought to the required pressure just before trial by means of a Gaede box pump. Ignition was effected by either a spark from a Sanax 20-inch coil or an electrically heated helix of platinum wire. The former was more suitable for the production of ordinary flames, and the latter for cool flames. Care had to be taken to use the appropriate means of ignition in any particular case. The flames given within the range ABCD were all of the cool variety and had to be observed in a darkened room. The cool-flame results were determined only to the nearest whole number. The results were all determined at 14—19°, and are given as percentages by volume.

| Original pressure of ether–air mixture (mm. Hg). | Ranges of ether–air that would propagate flame horizontally. |
|---|---|
| 758 | 1·88—34 |
| 660 | —35 |
| 590 | 1·87—35 |
| 500 | 1·88— 9·25 and 13—33 |
| 440 | — and 15—31 |
| 400 | 1·88— 8·4 and 19—27 |
| 360 | 1·89— 8·1 No cool flame detected. |
| 300 | — 7·5 |
| 240 | 1·98— |
| 190 | 2·05— 6·9 |
| 90 | 2·32— 6·1 |

I desire to thank Messrs. Nobel Industries, Ltd., and particularly Mr. W. Rintoul, Manager of the Research Section, for facilities accorded me for carrying out this work.

The Nobel Laboratories, Ardeer. [*Received, December 4th*, 1926.]

# LXXIV.—*Aromatic Thionyl and Chlorothionyl Derivatives. Part I. Thionylpyrocatechol and Dichlorothionylquinol.*

By ALBERT GREEN.

THIS paper is the first of a series in which it is proposed to deal primarily with the thionyl and the chlorothionyl compounds of hydroxybenzenes and, in particular, to study quantitatively their decomposition by weak organic acids, with a view to apply the information obtained to the more complex anthraquinone derivatives (J., 1924, **125**, 1450; 1926, 2198).

In the anthraquinone series two types of decomposition have been observed: one, which will be termed the *acyl decomposition*, is undergone by thionylalizarin, which is quantitatively converted by such acids into the 2-acyl derivative (I); the other type, the *hydroxylic decomposition*, is exemplified by thionylhystazarin, which reverts entirely to the hydroxy-compound (II). 2 : 3-Thionylanthragallol represents an intermediate case and gives a mixture of anthragallol and a monoacyl derivative.

(I.) $C_{14}H_6O_2\langle{}^{O}_{O}\rangle SO \longrightarrow C_{14}H_6O_2\langle{}^{OH}_{O\cdot COR}$

(II.) $C_{14}H_6O_2\langle{}^{O}_{O}\rangle SO \longrightarrow C_{14}H_6O_2\langle{}^{OH}_{OH}$

Repetition of the method employed by Anschütz and Posth (*Ber.*, 1894, **27**, 2752) in the preparation of thionylpyrocatechol (" catechol sulphite ") showed that the solid by-products mentioned by them form the greater part of the yield. A method of preparation resembling that used by Richter (*Ber.*, 1916, **49**, 2339) in the preparation of some thionyl derivatives of monohydric phenols was adopted.

Thionylpyrocatechol is much more stable to moisture than thionylalizarin, but after exposure to the air for 6 days it reverts completely to the hydroxy-compound. It reacts very slowly with acetic acid or acetic anhydride, even when heated under pressure at 180°, but the addition of a trace of pyridine to the boiling acid solution results in its complete conversion into *monoacetylpyrocatechol*. This compound affords a means of obtaining mixed diacyl derivatives, one of which, *acetylbenzoylpyrocatechol*, is described. With acetic anhydride and a little pyridine, thionylpyrocatechol gives diacetylpyrocatechol in quantitative yield.

Attempts to prepare a chlorothionyl derivative of quinol in the

presence of solvents gave stable, complex products which were analysed but not further investigated. Eventually *dichlorothionylquinol* was obtained as extremely unstable, white crystals which could be preserved only under thionyl chloride; when kept in sealed tubes for 2 days, they liquefied and considerable pressure was developed. In the air the dichlorothionyl compound fumed copiously and was rapidly converted into quinol; with boiling acetic acid or acetic anhydride it formed diacetylquinol in theoretical yield. *p*-Benzoquinone was recognised among the products of its complex auto-decomposition.

The acyl decomposition of dichlorothionylquinol was unexpected, since, in the conversion of 1 : 2-thionyl-7-chlorothionylanthrapurpurin (*loc. cit.*, p. 2198) into a monoacetylanthrapurpurin by acetic acid, the evidence points to the replacement of the chlorothionyl group by hydrogen.

Attempts to prepare thionyl and chlorothionyl derivatives of resorcinol yielded stable, high melting, insoluble products which analyses showed to be very complex. Richter (*loc. cit.*, p. 2345) states that he obtained the " sulphites " of several phenols including resorcinol, but he gives neither descriptions of the compounds nor analytical data. The author has carried out many preparations under various conditions, and has carefully repeated Richter's method several times, without obtaining such a compound. If indeed a simple derivative is obtainable, resorcinol would be expected to give a dichlorothionyl rather than a thionyl compound.

## Experimental.

*Thionylpyrocatechol*, $C_6H_4<^{O}_{O}>SO$.—To a cooled solution (10°) of 30 g. (1 mol.) of pyrocatechol in 150 c.c. of dry carbon disulphide and 43·0 c.c. (2 mols.) of pyridine, were added, with continuous stirring, 20·3 c.c. (1 mol.) of freshly-distilled thionyl chloride in 80 c.c. of dry carbon disulphide. After standing at 10° for 30 minutes, the mixture was boiled on the water-bath for a similar time. While still warm, the faintly yellow carbon disulphide solution was decanted from the syrupy layer of pyridine hydrochloride, which was washed several times with small quantities of the warm solvent. The carbon disulphide solution and washings were concentrated on the water-bath, and the last traces of the solvent were removed in a vacuum over paraffin wax. Thionylpyrocatechol (41 g.) was thus obtained as a faintly yellow, mobile liquid, b. p. 137—138°/105 mm. (Found : S, iodometrically as sulphur dioxide in the solution in aqueous sodium hydroxide, 20·3, 20·4. Calc. : S, 20·5%).

*Decomposition with acetic acid.* (A) A solution of thionylpyrocatechol in acetic acid, after boiling for 12 hours, still contained unchanged sulphite. This was shown by stirring the solution into water and washing the insoluble portion thoroughly; the alkaline solution of this decolorised acidified iodine solution.

(B) *Monoacetylpyrocatechol*, $OH{\cdot}C_6H_4{\cdot}OAc$. A solution of 16 g. of thionylpyrocatechol in 40 c.c. of glacial acetic acid and 3 drops of pyridine was boiled for 6 hours; evolution of sulphur dioxide was then no longer appreciable. The *monoacetyl* derivative was obtained by fractional distillation as a colourless, viscous liquid (14 g.), b. p. 189—191°/102 mm. In a freezing mixture, it set to a felted mass of thin, white plates, which, after draining on a porous tile, melted at 57—58°, were soluble in cold water, and gave a bottle-green colour with ferric chloride (Found: C, 63·0; H, 5·3; $CH_3{\cdot}CO$, 28·0. $C_8H_8O_3$ requires C, 63·2; H, 5·3; $CH_3{\cdot}CO$, 28·3%).

*Acetylbenzoylpyrocatechol*, $OAc{\cdot}C_6H_4{\cdot}OBz$. A solution of 7·0 g. (1 mol.) of monoacetylpyrocatechol in 10 c.c. of pyridine was treated with 5·5 c.c. (1 mol.) of benzoyl chloride, and after warming slightly, was stirred into cold dilute hydrochloric acid. The oily precipitate was separated, washed thoroughly with cold water, and taken up in ether. *Acetylbenzoylpyrocatechol* was obtained from the dried ethereal solution as a thick syrup (11 g.) which slowly solidified in fine, white needles, m. p. 78°. After recrystallisation from light petroleum–acetone it showed the same melting point (Found: C, 70·1; H, 4·7; $CH_3{\cdot}CO$, 16·7. $C_{15}H_{12}O_4$ requires C, 70·3; H, 4·7; $CH_3{\cdot}CO$, 16·8%). The substance is easily soluble in the cold in the common organic solvents except light petroleum, insoluble in water, and its alcoholic solution gives no colour with ferric chloride.

*Diacetylpyrocatechol.* Thionylpyrocatechol (5. g.) in acetic anhydride (15 c.c.) containing one drop of pyridine was boiled until sulphur dioxide was no longer evolved (40 minutes). The solution, when stirred into cold water, gave a white solid (6·5 g.), which crystallised from rectified spirits in short, white rods melting at 64° alone and when mixed with pure diacetylpyrocatechol (Found: $CH_3{\cdot}CO$, 44·3. Calc.: $CH_3{\cdot}CO$, 44·3%).

*Dichlorothionylquinol*, $C_6H_4(O{\cdot}SOCl)_2$.—Ice-cold thionyl chloride (200 c.c.) was added slowly to a mixture of quinol (40 g.) and pyridine (3 drops) contained in a flask fitted with a ground-in reflux condenser. Reaction commenced in the cold with evolution of hydrogen chloride, and was allowed to proceed at 15° for 2 hours; a dark orange-coloured solution had then been formed, This was boiled on the water-bath for 3 hours, concentrated to about 120 c.c., and kept dry.

The small, white crystals (about 30 g.) which separated were filtered off as required, and rapidly washed with dry benzene and absolute ether. They melted at 75° to a pale orange liquid (Found : C, 26·6, 26·4; H, 1·6, 1·7; * S, 23·2, 23·3; Cl, 25·7, 25·7. $C_6H_4O_4Cl_2S_2$ requires C, 26·2; H, 1·5; S, 23·3; Cl, 25·8%). By decomposition by the moisture of the air, followed by drying in a vacuum over sulphuric acid, 3·0026 g. of dichlorothionylquinol gave 1·1990 g. of quinol (theory requires 1·2010 g.), and 1·1240 g. yielded 0·4482 g. (theory requires 0·4496 g.). These products melted at 169° either alone or when mixed with pure quinol.

*Dichlorothionylquinol* fumes copiously in the air, and becomes yellow within one minute. It reacts violently with water and with aqueous and alcoholic solutions of potassium hydroxide. Even when stored in a dry atmosphere at room temperature, it decomposed to a complex mixture in which free sulphur was recognised.

*Thermal decomposition.* Dichlorothionylquinol was heated gradually from 70° to 150°. Decomposition commenced at about 95°. The sublimates were collected and yielded the characteristic yellow needles of *p*-benzoquinone, which was recognised by its odour and m. p. (116°, either alone or mixed with an authentic specimen). A small quantity of white, feathery crystals, m. p. 135°, which sublimed at a higher temperature than the quinone were not obtained in sufficient amount for analysis. The residue in the tube yielded no recognisable substance.

*Decomposition with acetic acid.* A solution of 4·0 g. of dichlorothionylquinol in 10 c.c. of glacial acetic acid was boiled for 15 minutes; hydrogen chloride and sulphur dioxide were then no longer perceptible at the mouth of the flask. When cold, the solution deposited 1·8 g. of lustrous, white plates of diacetylquinol (0·8 g. also was obtained by stirring the filtrate into water), m. p. 122°, alone and when mixed with the pure substance (Found : $CH_3{\cdot}CO$, 44·4. Calc. : $CH_3{\cdot}CO$, 44·3%).

*Decomposition with acetic anhydride.* The red solution of 2 g. of the dichlorothionyl compound in 5 c.c. of acetic anhydride, when boiled rapidly, became pale orange and evolved hydrogen chloride and sulphur dioxide very vigorously. After 8 minutes, the solution was cooled, and deposited white plates (0·8 g.) of diacetylquinol which, alone or mixed with an authentic specimen, melted at 123° (Found : $CH_3{\cdot}CO$, 44·1. Calc. : $CH_3{\cdot}CO$, 44·3%).

* Owing to the unstable nature of the compound, better analyses for carbon and hydrogen were not obtained, although both lead chromate and silver gauze were used in the combustion tubes. Satisfactory results for sulphur and chlorine were given by the Carius method.

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# LXXV.—*The Synthesis of* meso-*Alkyl and* meso-*Aryl Anthracene Derivatives. Part I.*

By EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and IVOR GRAY NIXON.

THE interest which attaches to the three-carbon transannular tautomerism exhibited by certain *meso*-alkyl anthracenes (Barnett, Cook, Matthews, *Ber.*, 1926, **59**, 1429, 2863) has rendered it desirable to review the methods available for the preparation of these compounds. Such methods fall roughly into two classes according as the *meso*-substituent is attached prior or subsequent to the closing of the central ring of the anthracene complex. The present communication deals with the former class of reaction.

(*A*). By treating methyl triphenylmethane-*o*-carboxylate with magnesium phenyl bromide, Haller and Guyot (*Bull. Soc. chim.*, 1904, **31**, 979) obtained a product which, when treated with hydrogen chloride in glacial acetic acid, passed into 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene (II).

(I.) $C_6H_4<\begin{matrix}CHPh_2\\CPh_2\cdot OMe\end{matrix}$ $\qquad$ $C_6H_4<\begin{matrix}CHPh\\CPh_2\end{matrix}>C_6H_4$ (II.)

They described their product as a methyl ether (I), but offered no evidence of the presence of the methoxyl group other than ultimate analysis, which in this case is totally insufficient to differentiate between the free hydroxy-compound and its methyl ether (Found: C, 89·7; H, 6·2. $C_{32}H_{26}O$ requires C, 90·1; H, 6·1. $C_{33}H_{28}O$ requires C, 90·0; H, 6·4%), and it has now been found that the compound is, as would be expected, the free hydroxy-compound, since identical products are obtained from the methyl and the ethyl ester.

With diphenylmethane-*o*-carboxylic acid (*o*-benzylbenzoic acid), which is easily accessible, a synthesis similar to the above might be expected to take place. To a limited extent this is true, as the esters of this acid, on treatment with magnesium phenyl bromide, yield an oily product (undoubtedly III) which is easily and almost quantitatively dehydrated to 9 : 9-diphenyl-9 : 10-dihydroanthracene (IV). Attempts to extend this synthesis by replacing the

magnesium phenyl bromide by magnesium ethyl, *iso*propyl or naphthyl bromide or by magnesium benzyl chloride were not successful, as no crystalline substance could be obtained from the viscid products of the reaction.

The hydroxy-compound (III) is not the sole product of the action of magnesium phenyl bromide on the esters of *o*-benzylbenzoic acid, a second product being formed at the same time to which formula (V) is given, this formula being based on analysis and molecular-weight determinations, the oxidation of the substance to *o*-dibenzoylbenzene, and on the fact that its formation is independent of the alcoholic radical (methyl, ethyl, or phenyl) in the ester.

(III.) $C_6H_4<\begin{matrix}CH_2Ph\\CPh_2\cdot OH\end{matrix}$ $\qquad$ $C_6H_4<\begin{matrix}CH_2\\CPh_2\end{matrix}>C_6H_4$ (IV.)

(V.) $C_6H_4<\begin{matrix}CH_2Ph\\CPh(OH)\cdot\end{matrix}\begin{matrix}PhH_2C\\CPh(OH)\end{matrix}>C_6H_4$

This pinacol obviously originates by the reduction of the ketone (*o*-benzylbenzophenone) which must be the first product of the action of magnesium phenyl bromide on the esters of *o*-benzylbenzoic acid, and, although the reducing action of Grignard solutions is well known, this appears to be the first case recorded in which they have been found to cause pinacol condensation.

(*B*). By treating diphenylphthalide with magnesium phenyl bromide, Guyot and Catel (*Bull. Soc. chim.*, 1906, **35**, 551, 562) obtained a compound which they described as a hydroxyphthalan (VI, R = Ph), tetraphenylphthalan (VIII) being obtained by employing a large excess of the Grignard solution (Schlenk and Brauns, *Ber.*, 1915, **48**, 727).

$C_6H_4<\begin{matrix}CR_2\\CPh(OH)\end{matrix}>O$ (VI.) $\qquad$ $C_6H_4<\begin{matrix}CR_2\cdot OH\\COPh\end{matrix}$ (VII.) $\qquad$ $C_6H_4<\begin{matrix}CPh_2\\CPh_2\end{matrix}>O$ (VIII.)

Guyot and Catel's compound cannot be dehydrated to give diphenylanthrone by treatment either with hydrogen chloride in glacial acetic acid or with concentrated sulphuric acid, but it does give diphenylanthrone on heating to 300°.

Similar compounds (R = Me or Et) are obtained by the action of magnesium phenyl bromide on dimethyl- and diethyl-phthalide; these, however, on heating do not pass into the corresponding dialkylanthrones, but lose water in a different direction to give unsaturated substances which are probably represented by formulæ (IX) and (X), although the possibility that they may be indene derivatives (*e.g.*, XI) is not excluded.

$C_6H_4<\begin{matrix}CMe{:}CH_2\\COPh\end{matrix}$ (IX.) $\qquad$ $C_6H_4<\begin{matrix}CEt{:}CHMe\\COPh\end{matrix}$ (X.) $\qquad$ $C_6H_4<\begin{matrix}CMe(OH)\\CPh\end{matrix}>CH$ (XI.)

No proof of the hydroxyphthalan structure (VI) is at present available, and the hydroxy-ketonic structure (VII) is suggested by Beilstein (" Handbuch," 4th Ed., Vol. VIII, p. 223). It is possible that the two formulæ may represent phases of an isodynamic change and it is proposed to investigate this point at a later date and at the same time to examine the dehydration products more closely. In the meantime the hydroxyphthalan structure is retained in the following, although the dehydration which takes place on heating is better explained by formula (VII).

(*C*). Arylhydroxyphthalans (VI or VII) have been obtained from the esters of phthalic acid by Guyot and Catel (*loc. cit.*) and by Weiss and Heidrich (*Monatsh.*, 1924, **45**, 210). Shibata (J., 1909, **95**, 1449) treated diethyl phthalate with magnesium phenyl bromide and after purifying his product by distillation under reduced pressure (b. p. 280—295°/8 mm.) isolated a colourless, crystalline substance which he described as diphenylphenylenephthalan (XII), and he based certain conclusions concerning the structure of the benzene ring on its formation. The formula given by Shibata appeared in the highest degree improbable and repetition of his experiments has proved that this supposed phenylene compound is really diphenylanthrone (XIII), the formation of which is undoubtedly due to dehydration of the hydroxyphthalan (VI or VII) first formed.

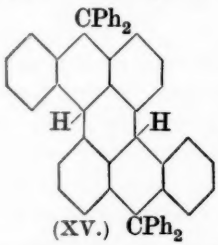
(XII.) $C_6H_4<\begin{matrix}CPh_2\\C(:C_6H_4)\end{matrix}>O$ $C_6H_4<\begin{matrix}CPh_2\\CO\end{matrix}>C_6H_4$ (XIII.)

Shibata's conclusions as regards the structure of the benzene ring are therefore valueless.

The action of magnesium phenyl bromide on *o*-dibenzoylbenzene also leads to the hydroxyphthalan (VI or VII) and from this to diphenylanthrone.

(*D*). Liebermann and Lindebaum (*Ber.*, 1905, **38**, 1804), by heating 9-bromo-10 : 10-diphenyl-9 : 10-dihydroanthracene (XIV) alone or with naphthalene, obtained a product which they described

$C_6H_4<\begin{matrix}CPh_2\\CHBr\end{matrix}>C_6H_4$
(XIV.)



(XV.)

$C_6H_4<\begin{matrix}CPh_2\\CH\end{matrix}>C_6H_4$
$C_6H_4<\begin{matrix}CH\\CPh_2\end{matrix}>C_6H_4$
(XVI.)

as tetraphenylheptacyclene and to which they gave formula (XV), without, however, bringing forward any experimental evidence in

its favour. The formation of a compound of this structure by the above reaction is not very probable, and an exactly similar, insoluble and highly stable substance is formed when diphenylanthrone is submitted to the pinacol reduction with zinc and hydrochloric acid in acetic acid solution, and also when 9 : 9-diphenyl-9 : 10-dihydroanthracene is heated to 250° in oxygen or is heated with benzal chloride or benzophenone chloride. Owing to the extreme insolubility of these substances and to the fact that they do not melt, it is impossible to state with certainty that they are identical, but it seems extremely probable that they are identical with the so-called tetraphenylheptacyclene and have formula (XVI). The impossibility of purifying them by recrystallisation renders it difficult to be certain that the molecule does not contain two hydrogen atoms less than the number required by the formula given ($C_{52}H_{38}$ requires C, 94·3; H, 5·7. $C_{52}H_{36}$ requires C, 94·6; H, 5·45%).

(*E*). Padova (*Ann. Chim.*, 1910, **19**, 400) found that dihydroanthracene condensed with benzophenone chloride to give bisdiphenylmethylenedihydroanthracene (XVII), the compound obtained by Staudinger (*Ber.*, 1908, **41**, 1362) by the action of diphenylketen on anthraquinone. 9 : 9-Diphenyldihydroanthracene behaves in the same way with benzophenone chloride and gives 9 : 9-diphenyl-10 : 10-diphenylmethylene-9 : 10-dihydroanthracene (XVIII), in which it has not been found possible to reduce the double bond.

(XVII.) $C_6H_4<\begin{matrix}C(:CPh_2)\\C(:CPh_2)\end{matrix}>C_6H_4$ $\quad$ $C_6H_4<\begin{matrix}CPh_2\\C(:CPh_2)\end{matrix}>C_6H_4$ (XVIII.)

Padova (*loc. cit.*) claimed to have reduced his compound by means of sodium and boiling benzyl alcohol, but we have not been able to repeat this.

## EXPERIMENTAL.

*ωω-Diphenyl-o-tolyldiphenylcarbinol.*—The methyl and *ethyl* esters of triphenylmethane-*o*-carboxylic acid were prepared in the usual way by esterification with the alcohol and hydrochloric acid. The former (m. p. 98°) has been prepared by Haller and Guyot (*loc. cit.*), by a different method. The latter, after being twice recrystallised from alcohol, formed a colourless, crystalline powder, m. p. 69° (Found : C, 83·2; H, 6·6. $C_{22}H_{20}O_2$ requires C, 83·5; H, 6·3%).

In each case, an ethereal solution of the ester was added to an ethereal solution of magnesium phenyl bromide (2 mols.) with cooling in a freezing mixture, and the whole was boiled for 4 hours and then poured on to a mixture of ice and solid ammonium chloride. The solid which separated and that which was obtained by distilling off the ether from the ethereal solution were identical and in each case, after recrystallisation from toluene–light petroleum, melted

at 218°, and a mixture of the specimens made from each ester showed no depression of melting point.

*o-Benzylbenzoic Acid.*—The statement by Ullmann (*Annalen*, 1896, **291**, 23) that *o*-benzoylbenzoic acid cannot be reduced beyond the phthalide stage by means of ammonia and zinc dust is incorrect, the following method having been found to be the most convenient one for the preparation of *o*-benzylbenzoic acid. Technical *o*-benzoylbenzoic acid (150 g.) was dissolved in 1 l. of concentrated ammonia (*d* 0·880) diluted with 300 c.c. of water, and a few c.c. of copper sulphate solution were added, followed by 300 g. of zinc dust in several portions with cooling. The whole was heated on the water-bath until a filtered sample, when acidified, gave a precipitate which was completely soluble in sodium carbonate (about 2 days). The filtrate and washings were then acidified with hydrochloric acid, and the precipitate was dissolved in sodium carbonate solution, reprecipitated with hydrochloric acid, and finally recrystallised from aqueous acetic acid. The yield was 117 g. of snow-white material, m. p. 118°.

Gresley (*Annalen*, 1886, **234**, 234) states that *o*-benzylbenzoic acid on treatment with sulphuric acid does not give anthrone but is oxidised to anthraquinone. This is erroneous, for when a solution of benzylbenzoic acid in concentrated sulphuric acid is kept for 2 hours at the ordinary temperature an almost quantitative yield of anthrone is obtained, and indeed this is a convenient method of preparing anthrone.

The *methyl* and *ethyl* esters were prepared in the usual way by means of the alcohol and hydrochloric acid and formed oils, b. p. 320° and 325°, respectively. The *phenyl* ester was obtained from the acid, phenol, and thionyl chloride in pyridine solution (Barnett and Nixon, *Chem. News*, 1924, **129**, 190) and was used in the crude state.

9 : 9-*Diphenyl*-9 : 10-*dihydroanthracene* (IV).—To an ethereal solution of magnesium phenyl bromide prepared from 8 g. of magnesium and 48 g. of bromobenzene and cooled in a freezing mixture, an ethereal solution of 32 g. of ethyl *o*-benzylbenzoate was added slowly. After boiling for an hour, or being kept at the ordinary temperature over-night, the whole was poured into ice and dilute hydrochloric acid, and the solid (15 g.; see below) collected. After washing and drying, the ether was removed from the ethereal solution. The viscid residue, which refused to crystallise, was heated for an hour on the water-bath with a glacial acetic acid solution of hydrogen chloride. The resulting diphenyldihydroanthracene (18 g.), m. p. 200°, was quantitatively oxidised to diphenylanthrone by chromic acid in glacial acetic acid.

Similar results were obtained when the methyl and the phenyl ester were used in place of the ethyl ester.

s-oo'-*Dibenzylbenzpinacol* (V).—The solid by-product insoluble in ether obtained as described above, after recrystallisation from benzene–light petroleum, chloroform–light petroleum, and methyl ethyl ketone, formed a colourless, crystalline powder, m. p. 175°. Its hot benzene solution showed a strong green fluorescence which vanished on cooling (Found: C, 87·8; H, 6·5; *M*, in ethylene dibromide, 540. $C_{40}H_{34}O_2$ requires C, 87·9; H, 6·2%; *M*, 546).

When 1 g. of the above pinacol in 20 c.c. of boiling glacial acetic acid was treated slowly with a concentrated aqueous solution of 3 g. of chromic acid, oxidation took place rapidly and, on cooling and dilution, a solid was obtained which, after recrystallisation, was identified as *o*-dibenzoylbenzene by direct comparison with an authentic sample.

Attempts to convert the pinacol into a dianthranyl derivative, an acetate, and a benzoate gave oily products only. The pinacol was not regenerated from these oils on boiling with alcoholic alkali, but they were converted into *o*-dibenzoylbenzene by oxidation with chromic acid. It is therefore likely that loss of water with formation of an α-pinacolin had taken place, but owing to the uninviting nature of the products the matter was not further investigated.

*Dimethylphenylhydroxyphthalan* (VI or VII; R = Me).—An ethereal solution of 8 g. of dimethylphthalide was added with water-cooling to an ethereal solution of magnesium phenyl bromide prepared from 2 g. of magnesium and 12 g. of bromobenzene. After boiling for 2 hours, the whole was poured on to ice and hydrochloric acid, and the ethereal layer was washed with sodium hydroxide solution and with water, dried over sodium sulphate, concentrated, and diluted with light petroleum. The m. p., 118°, of the resulting crystals (9·7 g.) was not altered by further recrystallisation from benzene–light petroleum (Found: C, 80·0; H, 6·8. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%).

o-iso*Propenylbenzophenone* (IX).—On distillation at atmospheric pressure, the above phthalan (10 g.) gave water and a product, b. p. 305°, which was dried in ethereal solution and distilled under reduced pressure; the yellow oil, b. p. 208—209°/45 mm., obtained became solid on cooling and after recrystallisation from aqueous alcohol formed colourless needles, m. p. 44° (Found: C, 86·2; H, 6·4. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%).

*o-iso*Propenylbenzophenone at once decolorised a solution of bromine in carbon tetrachloride. After 1 g. in 15 c.c. of glacial acetic acid had been boiled for an hour with addition of a concentrated aqueous solution of 5 g. of chromic acid, a solid was

obtained, on cooling and dilution, which was reprecipitated from its solution in aqueous sodium carbonate and then identified as *o*-benzoylbenzoic acid by direct comparison with an authentic sample.

*Diethylphenylhydroxyphthalan* (VI or VII; R = Et) was prepared from diethylphthalide and magnesium phenyl bromide in exactly the same way as the corresponding dimethyl derivative described above and formed colourless, glistening crystals, m. p. 94—95° (Found: C, 80·2; H, 7·5. $C_{18}H_{20}O_2$ requires C, 80·5; H, 7·5%). On heating, it lost water and passed into an unsaturated oil which was not further examined.

Attempts to prepare the dibenzyl analogue from dibenzylphthalide were not successful, most of the dibenzylphthalide being recovered unchanged.

*Action of Magnesium Phenyl Bromide on Ethyl Phthalate.*—The experiment was carried out essentially as described by Shibata (*loc. cit.*), and the product identified as diphenylanthrone by direct comparison with an authentic sample.

*Action of Magnesium Phenyl Bromide on* o-*Dibenzoylbenzene.*—Finely powdered *o*-dibenzoylbenzene (14·5 g.) was added with cooling to an ethereal solution of magnesium phenyl bromide prepared from 1·25 g. of magnesium and 8 g. of bromobenzene. After boiling for 6 hours, the whole was poured into ice and dilute sulphuric acid, unchanged *o*-dibenzoylbenzene (2·5 g.) removed by filtration, and the ether distilled off. The residue, after purification by distillation in steam and drying in ethereal solution, was heated at 300° for ½ hour, and after recrystallisation was identified as diphenylanthrone by direct comparison with an authentic sample.

In both the above preparations of diphenylanthrone it is probable that triphenylhydroxyphthalan (VI or VII; R = Ph) intervenes, as it was found that this substance passed into diphenylanthrone when heated at 300° for ½ hour. Dehydration to diphenylanthrone, however, could not be effected either with concentrated sulphuric acid or with hydrogen chloride in acetic acid.

*Tetraphenyltetrahydrodianthranyl* (XVI).—(*a*) Diphenylanthrone (4·4 g.) and 2·5 g. of zinc dust were boiled with 50 c.c. of glacial acetic acid, and 5 c.c. of fuming hydrochloric acid were added slowly. After 5 hours, the solid was collected, extracted with hydrochloric acid and with boiling glacial acetic acid, and then recrystallised from a very large volume of boiling nitrobenzene, in which, however, it was almost insoluble. The resulting cream-coloured powder did not melt at 320° (Found: C, 93·9; H, 5·75. $C_{52}H_{38}$ requires C, 94·3; H, 5·7%).

(*b*) Diphenyldihydroanthracene was heated for 2 hours in a

current of oxygen at 250°, and the product repeatedly extracted with boiling xylene to remove impurities. After being washed with ether and dried, it formed a colourless, crystalline powder which did not melt at 340° (Found: C, 94·3; H, 5·9%).

(*c*) An insoluble product similar to the above was obtained when diphenyldihydroanthracene was heated at 250° with benzal chloride.

9 : 9-*Diphenyl*-10 : 10-*diphenylmethylene*-9 : 10-*dihydroanthracene* (XVIII).—9 : 9-Diphenyl-9 : 10-dihydroanthracene (6·6 g.) and benzophenone chloride (5 g.) were heated for 2 hours at 250°, and coloured resinous by-products removed by washing with ether. The residual solid (7·8 g.) was dissolved in boiling xylene, and a small amount of an insoluble substance (probably tetraphenyltetrahydrodianthranyl) removed by filtration. On cooling, a colourless, crystalline powder separated which, after further recrystallisation, melted at 286° (Found: C, 94·0; H, 5·8. $C_{39}H_{28}$ requires C, 94·4; H, 5·6%).

The above compound was recovered unchanged after attempts to reduce it with zinc and hydrochloric acid in boiling glacial acetic acid, with sodium in boiling amyl and benzyl alcohols, and with hydriodic acid and red phosphorus at 180° for 7 hours.

10-*Chloro*-9 : 9 : 10-*triphenyl*-9 : 10-*dihydroanthracene*.—Five g. of triphenyldihydroanthranol (m. p. 204°, prepared from diphenylanthrone and magnesium phenyl bromide as described by Haller and Guyot, *Compt. rend.*, 1904, **139**, 9, but without the use of benzene as a solvent) were dissolved in 25 c.c. of benzene, and dry hydrogen chloride passed through the boiling solution for 20 minutes. On cooling and addition of ether, a solid was obtained which, after recrystallisation from benzene–ether, formed a colourless powder, m. p. 193—194°. It contained solvent of crystallisation which it lost at 120° (Found: Cl, 8·0. $C_{32}H_{23}Cl$ requires Cl, 8·0%). This chloro-compound, when boiled in benzene solution with copper powder in an atmosphere of carbon dioxide, gave a yellow solution which became more deeply coloured on heating. This solution probably contained a free radical, but further investigation has been postponed pending the publication of the work of another investigator.

9 : 9 : 10-*Triphenyl*-9 : 10-*dihydroanthracene* (II).—The preparation of this compound by the reduction of triphenyldihydroanthranol with zinc dust and acetic acid as described in the literature gave poor results, and it was found much better to reduce 15 g. of triphenyldihydroanthranol in 150 c.c. of boiling amyl alcohol by the addition of 7·5 g. of sodium. The solid which separated when the hot liquid was poured into water was washed with alcohol

and, after recrystallisation from benzene–alcohol (yield, 12 g.), melted at 230° (the m. p. given in the literature is 220°).

9 : 10-*Diphenyl*-9 : 10-*dihydroanthracene* was obtained most conveniently by reducing 1 g. of 9 : 10-diphenylanthracene in 25 c.c. of boiling amyl alcohol by the addition of 1 g. of sodium. The solution at first became yellow, but the yellow colour subsequently vanished with the fluorescence. The mixture was poured into water, the amyl alcohol removed with steam, and the product recrystallised from benzene–light petroleum.

*Action of Aluminium Chloride on* 9 : 9-*Diphenyl*-9 : 10-*dihydroanthracene*.—Diphenyldihydroanthracene (5 g.) and aluminium chloride (10 g.) were boiled for 6 hours with 50 c.c. of carbon disulphide. After decomposition with dilute hydrochloric acid, the carbon disulphide solution was washed with water, the solvent removed by distillation, and the product recrystallised from acetic acid and from alcohol. It then melted at 155—157°, alone or when mixed with an authentic sample of 9-phenylanthracene.

By the action of aluminium chloride on 9 : 10-diphenyl-9 : 10-dihydroanthracene, a product was obtained, m. p. 215—220°, which appeared to consist chiefly of 9 : 10-diphenylanthracene, since it did not depress the melting point of this substance; repeated recrystallisation, however, failed to raise the melting point.

The action of aluminium chloride on 9 : 9 : 10-triphenyl-9 : 10-dihydroanthracene in the cold led only to the recovery of the unchanged material, although the fluorescence of the solution and the low melting point of the crude recovered material indicated that re-establishment of the " bridge " had taken place to a slight extent. When the experiment was carried out in boiling carbon disulphide solution, only resinous products were obtained.

The authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed some of the expenses of this research.

Sir John Cass Technical Institute,
Jewry Street, E.C.3. [*Received, December 29th*, 1926.]

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## LXXVI.—*The Complex Chlorides of Tervalent Molybdenum.*

By William Ralph Bucknall, Sydney Raymond Carter, and William Wardlaw.

By the addition of the appropriate alkali chloride to electrolytically reduced solutions of tervalent molybdenum, Chilesotti (*Atti R. Accad. Lincei*, 1903, [v], 12, ii, 67) isolated the salts $K_3MoCl_6$ and

$R_2MoCl_5,H_2O$, where R = $NH_4$, Rb, and Cs. These represent two types of compounds common among tervalent elements. The conditions under which one or other type of salt could be obtained with certainty were not apparent to this investigator, but a recent research by Foerster and Fricke (*Z. angew. Chem.*, 1923, **36**, 458), in which they prepared $R_3MoCl_6$ and $R_2MoCl_5,H_2O$, where R = $NH_4$, K, Rb, or Cs, indicates, as would be expected, that the principal factor is acid concentration. So far, only an examination of their general reactions has been attempted. In view of the fact that they can be considered as co-ordination compounds, $R_3[MoCl_6]$ and $R_2[MoCl_5,H_2O]$, in which molybdenum exhibits a co-ordination number of six, it seemed of interest to determine whether such a formulation was justified.

The results obtained from physico-chemical determinations confirmed the above formulations for the salts, and at the same time furnished information as to the stability of the complex anion and the varying changes which the compounds undergo in aqueous solution.

## Experimental.

*Tripotassium Molybdenum Hexachloride.*—The method of preparation was that of Chilesotti (*loc. cit.*). 350 C.c. of a solution of molybdenum trioxide (35 g.) in 8*N*-hydrochloric acid were reduced to the tervalent condition, concentrated to 150 c.c. (33% $MoCl_3$) and saturated with hydrogen chloride. One-half to three-quarters of the theoretical amount of pure potassium chloride (30—40 g.) was added as a 10% solution in air-free water and the mixture concentrated at 70° under reduced pressure, until crystallisation commenced. The liquid was now filtered and the filtrate saturated with hydrogen chloride until cold, whereupon the double salt separated. The crystals were washed with concentrated hydrochloric acid, alcoholic hydrochloric acid, and finally with alcohol, and dried in a vacuum.

*Analysis.* The molybdenum was precipitated as sulphide (J., 1924, **125**, 1911), ignited, and weighed as the trioxide. The chloride in the filtrate and washings was estimated as silver chloride. The potassium was weighed as potassium sulphate (Found: Mo, 22·5; Cl, 50·2; K, 27·3. $K_3MoCl_6$ requires Mo, 22·5; Cl, 49·9; K, 27·5%).

*Dipotassium Molybdenum Pentachloride.*—This salt was isolated by Foerster and Fricke (*loc. cit.*) who, however, gave neither analyses nor details of preparation. The following method gave a satisfactory yield. 100 C.c. of the red solution containing tervalent molybdenum, prepared by the electrolysis of molybdenum trioxide (10 g. $MoO_3$) in 100 c.c. of 8*N*-hydrochloric acid, were added to

25 c.c. of a solution of potassium chloride (1 g.) and the mixture was concentrated in an air-free flask at 60—70° under reduced pressure to a volume of about 20 c.c. Air-free, absolute alcohol was now admitted and a bright brick-red crystalline precipitate separated, which, after filtration and washing with alcohol, was dried in a vacuum (Found: Mo, 26·0; Cl, 47·8. $K_2MoCl_5,H_2O$ requires Mo, 26·0; Cl, 48·0%). In attempting to isolate this compound from very dilute acid solutions, as suggested by Foerster and Fricke, an oxysalt was obtained (*q. v.*).

*Triammonium Molybdenum Hexachloride.*—Both Foerster and Fricke (*loc. cit.*) and Rosenheim and Li (*Ber.*, 1923, **56**, 2225) have prepared this salt, but in neither case were experimental details given. The formula assigned by Foerster and Fricke was $(NH_4)_3MoCl_6$, whilst the analyses of the other authors corresponded to $(NH_4)_3MoCl_6,2{\cdot}5H_2O$.

*Preparation.* 80 C.c. of the concentrated solution containing tervalent molybdenum (33% $MoCl_3$) were saturated with hydrogen chloride, added to a saturated aqueous solution of ammonium chloride (20 g.), and the mixture concentrated to the crystallising point. The diammonium molybdenum pentachloride thus formed was removed, and the filtrate again saturated with hydrogen chloride until cold. Small rose-coloured crystals separated which, after washing free from hydrochloric acid with aqueous alcohol, were dried in a vacuum.

*Analysis.* The molybdenum and chloride were estimated as above, and the ammonium by the distillation method. In this method, the ammoniacal distillate was titrated continuously against standard acid, using bromophenol-blue (0·04% solution) as indicator [Found: Mo, 25·2; Cl, 56·3; $NH_4$, 14·1. $(NH_4)_3MoCl_6,H_2O$ requires Mo, 25·2; Cl, 55·9; $NH_4$, 14·2%].

*Diammonium Molybdenum Pentachloride.*—This was prepared by the following method of Chilesotti: To 175 c.c. of the concentrated solution (33% $MoCl_3$) containing tervalent molybdenum, 25 g. of ammonium chloride as a 10% aqueous solution were added, and the mixture was concentrated at 70° under reduced pressure, until the salt crystallised as a bright brick-red compound [Found: Mo, 29·2; Cl, 54·4; $NH_4$, 11·0. $(NH_4)_2MoCl_5,H_2O$ requires Mo, 29·3; Cl, 54·2; $NH_4$, 11·0%].

*Cæsium and Rubidium Salts.*—These were prepared from solutions of the above salts by double decomposition with the alkali chlorides. They were also obtained by the addition of the corresponding alkali chlorides to the concentrated solution containing tervalent molybdenum and subsequent evaporation. Salts of the type $R_3MoCl_6$ were prepared in a similar manner from more concentrated

acid solutions (Found : Mo, 21·0; Cl, 38·6. $Rb_2MoCl_5,H_2O$ requires Mo, 20·8; Cl, 38·4%. For $Cs_2MoCl_5,H_2O$, found : Mo, 17·4; Cl, 32·1. Calc. : Mo, 17·2; Cl, 31·8%. For $Rb_3MoCl_6$, found : Mo, 16·9; Cl, 37·4. Calc. : Mo, 17·0; Cl, 37·7%. For $Cs_3MoCl_6$, found : Mo, 13·5; Cl, 29·9. Calc. : Mo, 13·6; Cl, 30·1%).

*General Properties of the Complex Salts.*—The salts of potassium and ammonium are extremely soluble even in cold water and give intensely red solutions. The salts of cæsium are quite insoluble and those of rubidium nearly so. In alcohol and ether all are practically insoluble. The aqueous solutions have an acid reaction, due to hydrolysis, which is accelerated by warming and results ultimately in the precipitation of the hydroxide of molybdenum. All the salts have pronounced reducing properties.

### *Physico-chemical Measurements.*

*Molecular-weight Determinations.*—The molecular weight was determined by the depression of the freezing point of air-free water. If $K_3[MoCl_6]$ represents the correct formulation for tripotassium molybdenum hexachloride, four ions should be present in solution, and the apparent molecular weight, when ionisation is complete, should be 106·6; whilst diammonium molybdenum pentachloride, represented by $(NH_4)_2[MoCl_5,H_2O]$, should yield three ions and give an apparent molecular weight of 109·2.

TABLE I.

| G. of substance per 100 g. water. | Conc. in mols. per 1000 g. water. | Osmotic factor. | Apparent mol. wt. |
|---|---|---|---|
| **Tripotassium molybdenum hexachloride.** | | | |
| 0·498 | 0·01170 | 3·86 | 110·3 |
| 0·829 | 0·01947 | 3·68 | 116·0 |
| 1·470 | 0·03453 | 3·54 | 120·5 |
| 3·045 | 0·07153 | 2·55 | 167·0 |
| **Diammonium molybdenum pentachloride.** | | | |
| 0·863 | 0·02635 | 3·10 | 105·6 |
| 1·484 | 0·04532 | 2·92 | 112·2 |
| 2·115 | 0·06460 | 2·81 | 116·8 |
| 5·391 | 0·1646 | 2·31 | 141·7 |

The results (Table I) furnish strong evidence in favour of the suggested formulations, although it was found that the substances underwent continuous hydrolysis in solution, as illustrated by the data (Table II) for a solution of tripotassium molybdenum hexachloride at a concentration of 0·07153 mol. per 1000 g. of water.

TABLE II.

| Time after dissolving (mins.) ..... | — | 10 | 30 | 37 | 45 | 53 | 73 | 155 |
|---|---|---|---|---|---|---|---|---|
| Apparent mol. wt. ... | 167·0 | 158·2 | 146·8 | 146·0 | 142·7 | 139·8 | 135·5 | 117·3 |
| Osmotic factor ..... | 2·55 | 2·70 | 2·91 | 2·92 | 2·99 | 3·05 | 3·18 | 3·64 |

After a considerable time, the hydroxide of molybdenum separated.

*Molecular-conductivity Determinations.*—Further evidence for the existence of these complex ions was obtained by determinations of the molecular conductivity. Whilst salts of the type $R_3MoCl_6$ gave results—immediately after dissolving—similar to those for a quaternary electrolyte, complexes of the type $R_2MoCl_5,H_2O$ were analogous to typical ternary electrolytes. Table III gives the values of $\mu$ for various dilutions at 1° when $t = 0$ min., and for comparison

TABLE III.

| | $K_3MoCl_6$. | | | | | $(NH_4)_3MoCl_6,H_2O$. | | |
|---|---|---|---|---|---|---|---|---|
| Dilution (litres per mol.) | 15·67 | 58·97 | 95·84 | 153·3 | 222·0 | 48·11 | 66·44 | 157·9 |
| $\mu$ | 155 | 195 | 220 | 230 | 245 | 208 | 210 | 225 |
| | $(NH_4)_2MoCl_5,H_2O$. | | | | | $K_2MoCl_5,H_2O$. | | |
| Dilution (litres per mol.) | 16·37 | 33·76 | 54·96 | 101·4 | 251·3 | 21·19 | 58·31 | 94·08 |
| $\mu$ | 107 | 110 | 132 | 140 | 175 | 113 | 140 | 142 |

the values of the molecular conductivities at 1° of typical salts are given in Table IV.

TABLE IV.

| Dilution (litres per mol.). | 16. | 32. | 64. | 128. | 256. |
|---|---|---|---|---|---|
| KCl. | 75·2 | 77·3 | 79·2 | 80·6 | 81·8 |
| $K_2SO_4$. | | | | 164 | 172 |
| $K_3Fe(CN)_6$. | 204·3 | 219·6 | 232·2 | 247·2 | 259·2 |
| $K_3W(CN)_8$. | 201·9 | 216·0 | 229·2 | 243·6 | 255·6 |
| $K_4Fe(CN)_6$. | | | | 292 | 316 |

However, as was anticipated from the molecular-weight determinations, the conductivities increased with time, as is seen from Figs. 1 and 2, in which molecular conductivities are plotted against time for various dilutions (as litres per mol., indicated as l./m.) of the two types of salt.

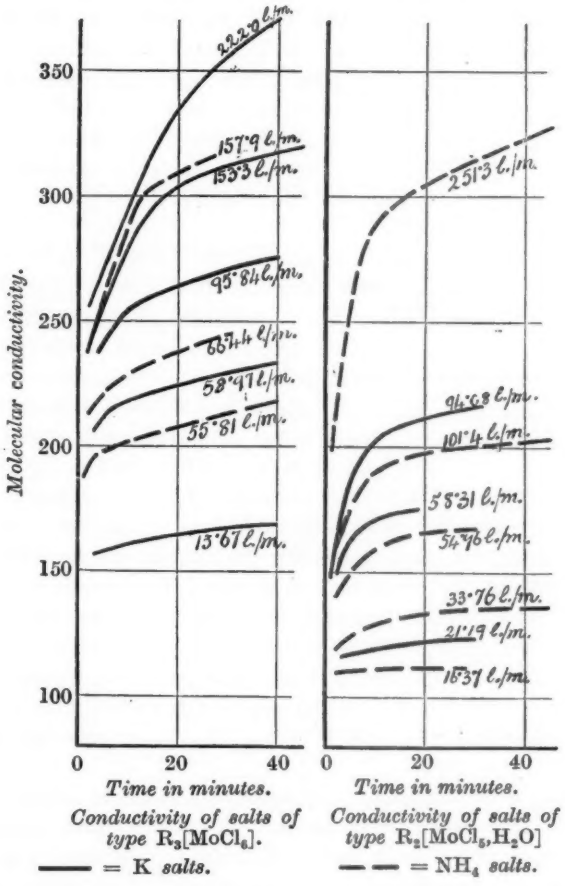
*Isolation of Double Salts of Molybdenyl Monochloride.*

It was noticed, during the preparation of tripotassium molybdenum hexachloride and in attempts to prepare dipotassium molybdenum pentachloride, that solutions containing tervalent molybdenum of a low acid concentration, tended to give rise to molybdenyl monochloride, which had previously been isolated from solutions of high molybdenum content, by precipitation in acetone (J., 1924, **125**, 2372).

*Preparation of Potassium Molybdenyl Dichloride.*—350 C.c. of the green solution containing tervalent molybdenum (35 g. $MoO_3$) were concentrated to *ca.* 120 c.c. and re-electrolysed for an hour to ensure that all the molybdenum was tervalent. 250 C.c. of a 10% solution of potassium chloride were then added and the whole was

concentrated nearly to dryness under reduced pressure at 70°. The red salt formed was then removed and the filtrate treated with alcohol, whereby a bright yellow substance was precipitated. This was filtered, washed with alcohol, and dried in a vacuum. It was slowly soluble in water to a reddish-brown solution and after a time

FIG. 1. FIG. 2.




the solid turned greenish-brown (Found: Mo, 36·0; Cl, 26·8; K, 14·3. $KMoOCl_2,2{\cdot}5H_2O$ requires Mo, 36·0; Cl, 26·6; K, 14·6%). The true hydrate is probably $KMoOCl_2,3H_2O$.

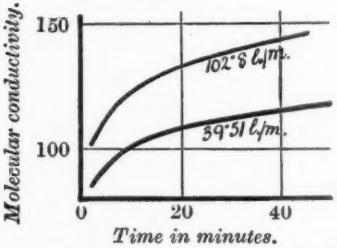
*Valency.* This was determined by titration with standard permanganate in the presence of manganous phosphate. The valency of the molybdenum is given by $(6 - 3w_1/w_2)$, where $w_1$ is the percentage of molybdenum calculated from the titration, assuming that

it is tervalent, and $w_2$ is the percentage of molybdenum found by gravimetric means. Here $w_1 = 35{\cdot}56$ and $w_2 = 36{\cdot}0$; hence the valency is 3.

*Conductivity at* 1°. The increase of molecular conductivity with time is illustrated in Fig. 3, with the same conventions as for Figs. 1 and 2. These results indicate, by analogy with potassium chloride (Table IV) that two ions are present in solution and that rapid hydrolysis occurs. Thus the new compound is shown to be $K[MoOCl_2,3H_2O]$.

By similar treatment of the green solution with ammonium chloride, a slightly impure substance was obtained, which was probably $(NH_4)[Mo(OH)Cl_3,2H_2O]$, and was shown to contain tervalent molybdenum.

FIG. 3.




*Conductivity of* $K[MoOCl_2,3H_2O]$.

*The Replacement of the Halogen Units in the Complex Salts.*

Chilesotti (*Gazzetta*, 1905, **34**, ii, 493), by double decomposition of the tripotassium molybdenum hexachloride and potassium thiocyanate, has prepared the complex salt $K_3Mo(CNS)_6$, whilst, by the action of hydrofluoric acid on the complex chlorides (Rosenheim and Li, *loc. cit.*), complex fluorides have been prepared. In view of the possibility of replacing the six chlorine atoms by three chelate groups such as the oxalato-, salicylato-, or phthalato-group the reactions between the complex chlorides and the alkali salts of oxalic, salicylic, and phthalic acids were investigated. In no case, however, was a complex salt obtained. Instead, the reactions yielded the co-ordination compounds $[Mo(OH)(OH{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2,H_2O]$ and $[Mo(OH)(O{\cdot}CO{\cdot}C_6H_4{\cdot}CO{\cdot}O),3H_2O]$ and an impure oxalate of the latter type.

*Reaction with Sodium Salicylate.*—A concentrated aqueous solution containing 2 g. (1 mol.) of diammonium molybdenum pentachloride and 1 g. (2 mols.) of sodium salicylate, was warmed to 70° in an atmosphere of nitrogen. The solution gradually darkened and finally became greenish-brown, a brown precipitate being formed. This was washed several times with air-free water in a nitrogen atmosphere and dried in a vacuum. The substance was dark-brown, insoluble in water, but soluble in alcohol giving a brown solution, and in alkaline hydroxides to a yellow solution.

The molybdenum was estimated by precipitation (as above) and also by direct ignition to the trioxide. The carbon and hydrogen

were estimated by combustion in oxygen [Found : Mo, 23·5; C, 41·5; H, 3·3. $Mo(OH)(OH{\cdot}C_6H_4{\cdot}CO{\cdot}O)_2,H_2O$ requires Mo, 23·7; C, 41·5; H, 3·2%].

The same compound results from the reaction between sodium salicylate and the other complex chlorides.

The solubility of this substance in alkaline hydroxides indicates a probable acidic structure, which can be represented by the co-ordination formula $[MoO,(O{\cdot}OC{\cdot}C_6H_4{\cdot}OH)_2,H_2O]H$, in which the molybdenum has a co-ordination number of six.

*Reaction with Disodium Phthalate.*—By warming equimolecular proportions of the complex salt and disodium phthalate in concentrated solution, a brown phthalate was prepared of which the analysis indicates the constitution $Mo(OH)[C_6H_4(CO{\cdot}O)_2],3H_2O$ (Found : Mo, 29·2; C, 29·1; H, 3·4. Calc. : Mo, 29·0; C, 29·0; H, 3·35%).

Like the salicylate, the new substance is insoluble in water and soluble in alkaline hydroxides, and probably has an acidic structure in accordance with the formulation $[MoO{\cdot}(C_6H_4(CO{\cdot}O)_2),3H_2O]H$.

*Reaction with Ammonium Oxalate.*—On warming a concentrated solution containing the complex salt and ammonium oxalate, the liquid turned brown and finally greenish-brown, but no insoluble compound was formed. The addition of the solution to alcohol resulted in the precipitation of a brown substance which, after freeing from ammonium chloride by washing with aqueous alcohol, gave analyses which showed that, although ammonium oxalate was still present as impurity, the substance was probably

$$Mo(OH)(C_2O_4),3H_2O,$$

identical with the oxyoxalate previously isolated (J., 1925, **127**, 1311).

*Reaction of the Complex Salts with Liquid Ammonia.*

Attempts to replace the chlorine in the red salts by the $NH_3$ group proved unsuccessful, but it was shown that diammonium molybdenum pentachloride takes up ammonia to give an unstable monoammine, which may be written as $(NH_4)_2[MoCl_5,NH_3]H_2O$.

About 15 c.c. of liquid ammonia were added to 2—3 g. of the above complex chloride contained in a dry tube surrounded by ether and solid carbon dioxide. The reaction mixture was well stirred and the supernatant liquid then decanted off. The remaining solid was treated similarly with a further quantity of liquid ammonia to extract any ammonium chloride formed. After repeated washing with dry acetone to remove excess of ammonia, the solid mass was dried in an evacuated desiccator containing calcium chloride, and immediately analysed [Found : Mo, 26·7; Cl, 49·6; $NH_4$, 15·1; $Mo : NH_4 : Cl = 1 : 3{\cdot}01 : 5{\cdot}03$. $(NH_4)_2MoCl_5,NH_3,H_2O$ requires

Mo, 27·9; Cl, 51·5; $NH_4$, 15·7. $(NH_4)_2MoCl_5,NH_3,2H_2O$ requires Mo, 26·5; Cl, 49·0; $NH_4$, 14·9%]. The true hydrate when freshly prepared is probably $(NH_4)_2[MoCl_5,NH_3]H_2O$.

This mauve-coloured ammine is extremely hygroscopic and undergoes rapid hydrolysis, ammonium chloride being liberated whilst the substance itself turns brown. It is readily soluble in water, producing a reddish-brown solution from which the hydroxide separates after a few minutes. It was therefore impossible to determine its molecular conductivity.

On treatment with concentrated hydrochloric acid, the ammine dissolved, producing a brilliant blue coloration. On dilution the solution turned green and finally pink, owing, in all probability, to the re-formation of the original red complex chloride, with liberation of ammonium chloride.

An attempt was made to isolate the blue substance by passing hydrogen chloride into the acid solution of the ammine, maintained at the low temperature of the mixture of solid carbon dioxide and ether. A greenish-blue substance was precipitated, which, after washing with alcohol to remove hydrochloric acid, turned greenish-grey. In water, it gave a greenish-blue solution, which rapidly turned pink. The analytical figures were not in agreement with any definite formula.

Liquid ammonia does not appear to react with the tripotassium molybdenum hexachloride, thus supporting the view that the ammonia replaces the molecule of water in diammonium molybdenum pentachloride.

*Discussion.*

The results of the physico-chemical measurements, together with the isolation of co-ordination compounds of the formulæ

$$K[MoOCl_2,3H_2O],\ [MoO,C_6H_4(CO\cdot O)_2,3H_2O]H$$

and $[MoO,(OH\cdot C_6H_4\cdot CO\cdot O)_2,H_2O]H$, can be explained on the assumption that the complex salts undergo ionisation and hydrolysis in accordance with the following scheme :

$$\begin{aligned}
R_3[MoCl_6] + H_2O &\rightleftharpoons R_2[MoCl_5,H_2O] + RCl.\\
R_2[MoCl_5,H_2O] + H_2O &\rightleftharpoons R[MoCl_4,2H_2O] + RCl.\\
R[MoCl_4,2H_2O] + H_2O &\rightleftharpoons MoCl_3,3H_2O + RCl.\\
MoCl_3,xH_2O &\rightleftharpoons MoCl_2(OH) + HCl + (x-1)H_2O.\\
MoCl_2(OH) &\rightleftharpoons MoOCl + HCl.
\end{aligned}$$

The existence of the double salts $R_3MoCl_6$ and $R_2MoCl_5,H_2O$ is evidence of the presence of $MoCl_3$; the salicylato- and phthalato-compounds are derived from the intermediate $MoCl_2(OH)$; whilst MoOCl and its complex salts have been isolated.

It is of interest to note, in the case of the complex chlorides $R_3MoCl_6$, $R_2MoCl_5,H_2O$, and $KMoOCl_2,3H_2O$, and also of the insoluble molybdenyl salicylate and phthalate, that the molybdenum atom is associated with 51 electrons, 3 less than the number required for an inert-gas structure. In this respect, molybdenum shows a close analogy to chromium in its complex salts.

Here is an excellent illustration of the fact that co-ordination compounds may be stable in cases where the central atom has not an inert-gas structure, provided that the associating units are regularly distributed. Nevertheless, the complex compounds of tervalent molybdenum do not exhibit the stability of the complex cyanides of quadrivalent molybdenum, $R_4[Mo(CN)_8]$, in which the central atom has an inert-gas structure.

The authors wish to express their thanks for the award of a Priestley Scholarship to one of them (W. R. B.) and to the Chemical Society and Messrs. Brunner Mond and Co., Ltd., for grants in aid of this investigation.

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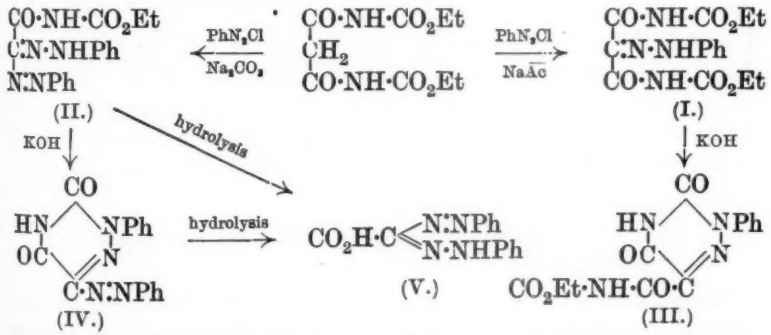
## LXXVII.—*The Reaction between Diazonium Salts and Malonyldiurethane.*

By MARTHA ANNIE WHITELEY and DOROTHY YAPP.

MALONYLDIURETHANE condenses with benzenediazonium salts, yielding the *hydrazone* (I) or the *formazyl* derivative (II) according to whether the reaction is carried out in the presence of acetic acid or sodium carbonate, respectively. Each of these compounds




undergoes internal condensation by the action of potassium hydroxide whereby alcohol is eliminated between the ethoxyl group

of the urethano-radical and the imino-hydrogen of the hydrazone group, yielding respectively the *carbourethane* (III) and the *benzeneazo-derivative* (IV) of 3 : 5-*diketo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine*. On hydrolysis with hot potassium hydroxide solution, the formazyl compound (II) and the benzeneazotriazine (IV) each yield formazylcarboxylic acid (V).

When the benzenediazonium salt in the above reactions is replaced by certain substituted derivatives, it is found that the nature of the substituent radical and its position in the benzene ring affect the course of the reaction: the *p*-toluene- and the *o*-nitrobenzene-diazonium salt each yield both the hydrazone and the formazyl compound, from which the triazine compounds can be obtained; whereas the *p*-nitrobenzenediazonium salt yields the hydrazone in two isomeric forms, but no formazyl compound, and each of the isomeric hydrazones yields the same triazine compound; *m*-nitrobenzenediazonium salt yields the hydrazone only, from which at present no triazine compound has been obtained.

In respect of forming a hydrazone and not an azo-compound by the action of benzenediazonium acetate, malonyldiurethane resembles malonic acid, barbituric acid and other compounds containing the keto-methylene group (compare Meyer, *Ber.*, 1888, **21**, 118; 1891, **24**, 1241; v. Pechmann, *Ber.*, 1892, **25**, 3175; Kuhling, *Ber.*, 1891, **24**, 4140; 1898, **31**, 1972; Bamberger and Wheelwright, *Ber.*, 1892, **25**, 3201), and this constitution of the compound was confirmed by its preparation from monobromomalonyldiurethane and phenylhydrazine, when simultaneous condensation and oxidation occurred (compare v. Pechmann, *loc. cit.*). That

$$(CO_2Et\cdot NH\cdot CO)_2CHBr \xrightarrow{PhNH\cdot NH_2} [(CO_2Et\cdot NH\cdot CO)_2CH\cdot NH\cdot NHPh] \downarrow (CO_2Et\cdot NH\cdot CO)_2C{:}N\cdot NHPh$$

this reaction is a general one was shown by the preparation of mesoxamide phenylhydrazone by condensation of (i) dibromomalonamide with phenylhydrazine as described by Ruhemann and Orton (J., 1895, **67**, 1003); (ii) monobromomalonamide with phenylhydrazine; and (iii) benzenediazonium acetate with malonamide:

$$\left.\begin{matrix}(CO\cdot NH_2)_2CBr_2\\(CO\cdot NH_2)_2CHBr\\(CO\cdot NH_2)_2CH_2\end{matrix}\right\} \xrightarrow[PhN_2Cl,NaAc]{PhNH\cdot NH_2} (CO\cdot NH_2)_2C{:}N\cdot NHPh.$$

The formation of the formazyl compound when benzenediazonium chloride is added to a solution of malonyldiurethane in sodium carbonate solution is probably due to the further action of the diazonium compound on the phenylhydrazone of glyoxalylurethane

produced by the hydrolysis of one of the carbourethano-groups and loss of carbon dioxide from the resulting acid :

$$(CO\cdot NH\cdot CO_2Et)_2C{:}N\cdot NHPh \xrightarrow{\text{hydrolysis}} (CO\cdot NH\cdot CO_2Et)C(CO_2H){:}N\cdot NHPh$$

$$(CO\cdot NH\cdot CO_2Et)C(N{:}NPh){:}N\cdot NHPh \xrightarrow{-CO_2} (CO\cdot NH\cdot CO_2Et)CH{:}N\cdot NHPh$$

$$(CO\cdot NH\cdot CO_2Et)CH{:}N\cdot NHPh \xrightarrow{PhN_2\cdot OH} (CO\cdot NH\cdot CO_2Et)CH{:}N\cdot NHPh$$

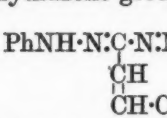
In respect of the above reactions, malonyldiurethane closely resembles malonic acid (v. Pechmann, *loc. cit.*; Busch and Wolbring, *J. pr. Chem.*, 1905, **72**, 366), but whereas the final product of the action of diazonium salts on malonic acid is formazylazobenzene, owing to the readiness with which formazylcarboxylic acid loses carbon dioxide, its urethane derivative resists hydrolysis and forms a stable six-membered ring by loss of alcohol.

There are numerous cases recorded in the literature of internal ring formation in hydrazones and formazyl compounds (see Bamberger and Lorenzen, *Ber.*, 1892, **25**, 3539; Bamberger and de Gruyter, *Ber.*, 1893, **26**, 2385, 2783; Bamberger and Witten, *Ber.*, 1894, **27**, 2786; v. Pechmann, *ibid.*, p. 1679; v. Pechmann and Runge, *ibid.*, p. 2920; Fichter and Schiess, *Ber.*, 1900, **33**, 747), but the researches of Henrich and his collaborators on the formazyl and arylazohydrazone derivatives yielded by glutaconic acid and its esters appear to have a direct bearing on the work described in this paper. These authors found that glutaconic acid reacts with benzenediazonium chloride (2 mols.) in the presence of sodium acetate to form formazylacrylic acid, $CO_2H\cdot CH{:}CH\cdot C(N{:}NPh){:}N\cdot NHPh$ (Henrich and Thomas, *Ber.*, 1907, **40**, 4924); whilst ethyl glutaconate under similar conditions reacts with the diazonium salt (1 mol.) to form a compound which has the constitution of the azo-compound, $CO_2Et\cdot CH{:}CH\cdot CH(CO_2Et)\cdot N{:}NPh$, or that of the tautomeric hydrazone, $CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}N\cdot NHPh$; and when an excess of the diazonium salt is used the arylazohydrazone, ethyl α-keto-γ-benzeneazoglutaconate phenylhydrazone,

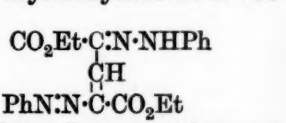
$$CO_2Et\cdot C(N{:}NPh){:}CH\cdot C(CO_2Et){:}N\cdot NHPh,$$

is formed, and this compound differs from the others in that it very readily loses a molecule of alcohol, even on boiling with alcohol, to form the ring compound, ethyl 1-phenyl-5-benzeneazopyridazin-6-one-3-carboxylate, $CH\leqslant\begin{matrix}C(CO_2Et)=N\\C(N{:}NPh)\cdot CO\end{matrix}>NPh$ (Henrich, Reichenburg, Nachtigall, Thomas, and Baum, *Annalen*, 1910, **376**, 125). In view of the readiness with which the phenylhydrazone of mesoxalyldiurethane and the urethane derivative of formazylglyoxylic acid form rings by the loss of alcohol, and in this respect resemble the arylazohydrazone derivative of ethyl glutaconate, it

is the more remarkable that formazylacrylic acid and its ethyl ester are such stable substances and show no tendency to form rings. A simple explanation of this anomalous behaviour would be afforded if it were assumed that the stable forms of these compounds have the *trans*-configuration in respect of the carbethoxy- and hydrazone-groups, whilst that of the arylazohydrazone is *cis*:



Ethyl *trans*-formazylacrylate.



Ethyl *cis*-α-keto-γ-benzeneazoglutaconate phenylhydrazone.

The stability of the first product of the action of diazonium acetate on ethyl glutaconate, a compound which can even be distilled without decomposition, may be regarded as evidence of its having the azo-structure, but if it is a hydrazone it probably has the *trans*-configuration.

With reference to the part played by the nature and position of the radical in substituted benzenediazonium derivatives in inhibiting the formation of formazyl derivatives from hydrazones, or of ring compounds from hydrazones or formazyl compounds, the evidence at present available is scanty and of a conflicting nature. The results obtained with malonyldiurethane indicate that a positive substituent in the ortho- or a negative substituent in the para-position offers no hindrance to the formation of the formazyl compound (II) or of the ring compound (III), but that a positive substituent in the para-position prevents the formation of the formazyl, but not of the ring compound, whilst a positive substituent in the meta-position inhibits both formazyl and ring formation. Busch and Wolbring (*loc. cit.*) found that malonic acid gives chiefly the substituted hydrazone of glyoxylic acid and very little of the formazyl hydride when it condenses with certain ortho-substituted derivatives of benzenediazonium salts, such as *o*-nitro-, *o*-chloro-, *o*-bromo-, or *o*-iodo-derivatives, whilst the formazyl compound is the only product when malonic acid condenses with *p*-bromo- or *m*-nitro-benzenediazonium salts, and the chief product when it condenses with *p*-nitroaniline. Henrich and his collaborators (*loc. cit.*), who studied the relative ease of ring formation in the substituted arylazohydrazones of ethyl glutaconate, found that it depended both on the nature and on the position of the substituent in the benzene ring. The more negative the substituent the more readily did ring formation occur, provided that the substituent was not in the ortho-position, as ortho-substitution presented a steric hindrance to the elimination of alcohol.

## EXPERIMENTAL.

I. *Phenylhydrazone of Mesoxalyldiurethane* (I).—(i) Into a solution of 5 g. (1 mol.) of malonyldiurethane in 200 c.c. of dilute aqueous sodium acetate cooled in ice, was slowly stirred a cold solution of benzenediazonium acetate prepared by diazotising 1·8 g. (1 mol.) of aniline dissolved in 10 c.c. of dilute hydrochloric acid (1 : 1) and adding excess of sodium acetate. The mixture was kept for 2 hours at 0—5° and the *hydrazone* separated in a crystalline form (yield, 4·8 g.). It is soluble in acetic acid, formic acid, or chloroform, but insoluble, or nearly so, in all the other ordinary organic solvents, and crystallises from acetic acid in pale yellow needles, m. p. 203° (decomp.) (Found: C, 51·3; H, 5·15; N, 16·1. $C_{15}H_{18}O_6N_4$ requires C, 51·4; H, 5·1; N, 16·0%).

(ii) The same compound was also prepared by heating at 100° an alcoholic solution of monobromomalonyldiurethane (1 mol.) and phenylhydrazine (1 mol.).

By replacing the aniline in preparation (i) above by its equivalent of the corresponding base, the following substituted phenylhydrazones of mesoxalyldiurethane were prepared:

(1) The o-*nitrophenylhydrazone*,

$$(CO{\cdot}NH{\cdot}CO_2Et)_2C{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

is soluble in acetic acid, acetone, or chloroform, sparingly soluble in ethyl or methyl alcohol or benzene, and insoluble in petroleum; it crystallises from acetic acid in thin, yellow needles, m. p. 208° (decomp.) (Found: N, 17·9. $C_{15}H_{17}O_8N_5$ requires N, 17·7%).

(2) The m-*nitrophenylhydrazone* is very readily soluble in acetic acid, but otherwise resembles the ortho-compound in its solubility. It crystallises from formic acid in very pale yellow needles, m. p. 215° (Found: N, 17·6%).

(3) The p-*nitrophenylhydrazone* crystallises from acetic acid in pale yellow needles, m. p. 218° (decomp.) (Found: N, 17·5%). An isomeric form of this hydrazone is obtained when the condensation of malonyldiurethane with *p*-nitrobenzenediazonium salt is effected in the presence of sufficient sodium carbonate to produce a neutral or slightly alkaline reaction. The *isomeride* crystallises in orange-coloured needles, m. p. 208° (decomp.) (Found: C, 45·4; H, 4·5; N, 17·8. $C_{15}H_{17}O_8N_5$ requires C, 45·5; H, 4·3; N, 17·7%).

(4) The p-*tolylhydrazone*, $(CO{\cdot}NH{\cdot}CO_2Et)_2C{:}N{\cdot}NH{\cdot}C_7H_7$, is readily soluble in all the usual organic solvents with the exception of petroleum; it crystallises from alcohol in pale yellow needles, m. p. 186° (Found: N, 15·5. $C_{16}H_{20}O_6N_4$ requires N, 15·4%).

II. *Urethane Derivative of Formazylcarboxylic Acid* (II).—Into a cold solution of 5 g. (1 mol.) of malonyldiurethane and 8·8 g. (2·5 mols.) of sodium carbonate in 200 c.c. of water was stirred

one-half of a cold solution of benzenediazonium chloride, prepared by diazotising 3·6 g. (2 mols.) of aniline in 20 c.c. of dilute hydrochloric acid (1 : 1). The mixture was kept cold and after 2 hours the red precipitate (4·1 g.) was removed by filtration and the filtrate treated with the remainder of the diazonium solution; a further quantity (1 g.) of the product was then obtained. The product consisted of the *urethane* derivative of *formazylcarboxylic acid* (II) containing a small quantity of the triazine compound (III); separation was effected by boiling with water, in which the triazine compound is soluble. The urethane derivative of formazylcarboxylic acid is soluble in all the usual organic solvents except petroleum, it crystallises from alcohol in bright red plates, m. p. 159° (decomp.), and it gives a deep purple coloration when dissolved in concentrated sulphuric acid (Found: C, 60·1; H, 5·1; N, 20·9. $C_{17}H_{17}O_3N_5$ requires C, 60·2; H, 5·0; N, 20·6%). It undergoes hydrolysis when boiled with 10% potassium hydroxide solution, yielding formazylcarboxylic acid (V), m. p. 162° (v. Pechmann, *Ber.*, 1892, **25**, 3175, gives m. p. 162—163°) (Found: C, 63·2; H, 4·6; N, 20·7. Calc.: C, 62·7; H, 4·5; N, 20·9%).

The following substituted formazyl derivatives were similarly prepared:

(1) The *urethane* derivative of *di*-o-*nitroformazylcarboxylic acid*, $CO_2Et{\cdot}NH{\cdot}CO{\cdot}C(N{:}N{\cdot}C_6H_4{\cdot}NO_2){:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, is soluble in all the ordinary organic solvents with the exception of petroleum, and of formic acid, in which it decomposes; it crystallises from acetic acid in red plates with a green reflex, containing acetic acid of crystallisation and melting at 105°, and develops a deep blue coloration when dissolved in concentrated sulphuric acid (Found: C, 46·8; H, 3·9; N, 19·9. $C_{17}H_{15}O_7N_7,C_2H_4O_2$ requires C, 46·6; H, 3·9; N, 20·0%).

(2) The *urethane* derivative of *di*-p-*tolylformazylcarboxylic acid*, $CO_2Et{\cdot}NH{\cdot}CO{\cdot}C(N{:}N{\cdot}C_7H_7){:}N{\cdot}NH{\cdot}C_7H_7$, resembles the *o*-nitro-derivative in its solubility, and crystallises from alcohol in bright red needles that melt at 153°, and give a deep blue coloration with concentrated sulphuric acid (Found: C, 62·3; H, 5·9; N, 19·1. $C_{19}H_{21}O_3N_5$ requires C, 62·15; H, 5·7; N, 19·1%). This compound is hydrolysed by boiling with 10% potassium hydroxide solution, yielding *di*-p-*tolylformazylcarboxylic acid*,

$$HO_2C{\cdot}C(N{:}N{\cdot}C_7H_7){:}N{\cdot}NH{\cdot}C_7H_7,$$

which crystallises from acetic acid in red, rhomboidal crystals, m. p. 182° (Found: N, 19·1. $C_{16}H_{16}O_2N_4$ requires N, 18·9%).

III. The *urethane* derivative of 3 : 5-*diketo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* (III) was prepared by dissolving the phenylhydrazone of mesoxalyldiurethane (I) in warm 10%

aqueous potassium hydroxide and subsequently acidifying the solution with a dilute mineral acid. It is soluble in hot water and crystallises from very dilute alcohol in pale buff-coloured, feathery crystals, m. p. 203° (decomp.) (Found: C, 51·7 *; H, 4·05; N, 18·5. $C_{13}H_{12}O_5N_4$ requires C, 51·3; H, 3·9; N, 18·4%).

The following substituted triazine derivatives were similarly prepared:

(1) The *urethane* derivative of 3 : 5-*diketo*-2-p-*nitrophenyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* is obtained from each of the two isomeric forms of the *p*-nitrophenylhydrazone of mesoxalyldiurethane; it crystallises in garnet-red prisms, m. p. 205° (Found: N, 19·9. $C_{13}H_{11}O_7N_5$ requires N, 20·05%).

(2) The *urethane* derivative of 3 : 5-*diketo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine*-6-*carboxylic acid* crystallises from dilute alcohol in pale buff, silky needles, m. p. 218° (decomp.) (Found: C, 53·0 *; H, 4·5; N, 17·6. $C_{14}H_{14}O_5N_4$ requires C, 52·9; H, 4·4; N, 17·6%).

IV. 3 : 5-*Diketo*-6-*benzeneazo*-2-*phenyltetrahydro*-1 : 2 : 4-*triazine* (IV) was prepared by two methods: (i) by dissolving the urethane derivative of formazylcarboxylic acid (II) in warm alcoholic potassium hydroxide, diluting the solution with water, and acidifying the mixture with dilute hydrochloric acid; (ii) by the prolonged boiling of the same formazyl compound in xylene solution. The *triazine* crystallises from alcohol in orange needles, m. p. 256° (decomp.), that develop a deep red colour when dissolved in concentrated sulphuric acid (Found: C, 61·9 *; H, 3·8; N, 24·0. $C_{15}H_{11}O_2N_5$ requires C, 61·4; H, 3·75; N, 23·9%). This compound is hydrolysed by boiling with 10% potassium hydroxide solution, yielding formazylcarboxylic acid, m. p. 162°.

The following substituted triazine derivatives were similarly prepared:

(1) 3 : 5-*Diketo*-2-o-*nitrophenyl*-6-o-*nitrobenzeneazotetrahydro*-1:2:4-*triazine* crystallises from acetic acid in red, rhomboidal crystals, m. p. 224° (decomp.) (Found: N, 25·4. $C_{15}H_9O_6N_7$ requires N, 25·6%).

(2) 3 : 5-*Diketo*-6-p-*tolueneazo*-2-p-*tolyltetrahydro*-1 : 2 : 4-*triazine* crystallises from alcohol in orange-red needles, m. p. 246° (Found: C, 64·3 *; H, 4·8; N, 21·75. $C_{17}H_{15}O_2N_5$ requires C, 63·55; H, 4·7; N, 21·8%). When this compound is hydrolysed by hot potassium hydroxide solution the ring is ruptured in two places and di-*p*-tolylformazylcarboxylic acid, m. p. 182°, is formed.

The phenylhydrazone of mesoxamide, $(CO{\cdot}NH_2)_2C{:}N{\cdot}NHPh$, was prepared by Ruhemann and Orton (J., 1895, **67**, 1005) by heat-

* The high values obtained for carbon in the analysis of triazine compounds have been observed by Widman (*Ber.*, 1893, **26**, 2612).

ing an alcoholic solution of dibromomalonamide with the required quantity of phenylhydrazine; it crystallises in long, yellow needles, m. p. 232—233°. The same compound was obtained (i) by heating an alcoholic solution of monobromomalonamide (Backes, West, and Whiteley, J., 1921, **119**, 364) with one equivalent of phenylhydrazine (Found: C, 51·9; H, 4·95; N, 27·2. Calc.: C, 52·4; H, 4·85; N, 27·2%); and (ii) by the action of benzenediazonium chloride on an aqueous solution of malonamide containing excess of sodium acetate; the product crystallised from alcohol in long, yellow needles that melted at 232° and did not depress the melting point of the compound prepared by Ruhemann and Orton's method.

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# NOTES.

*A Derivative of αα′α″-Triaminotrimethylamine.* By FREDERIC BARRY KIPPING and FREDERICK GEORGE MANN.

IT has been shown by Ristenpart (*Ber.*, 1896, **29**, 2530) that molten phthal-β-bromoethylimide when treated with gaseous ammonia gives triphthalimidotriethylamine, $(C_6H_4{:}C_2O_2{:}N{\cdot}C_2H_4)_3N$, which on hydrolysis with hydrochloric acid furnishes ββ′β″-triaminotriethylamine trihydrochloride, $N(C_2H_4{\cdot}NH_2,HCl)_3$. This preparation has been improved by Mann and Pope (*Proc. Roy. Soc.*, 1925, [*A*], **109**, 444), who have also prepared γγ′γ″-triaminotripropylamine tetrahydrochloride similarly from phthal-γ-bromopropylimide (J., 1926, 489).

We have now investigated the stability of αα′α″-triaminotrimethylamine, $N(CH_2{\cdot}NH_2)_3$, by a similar series of reactions. Phthalbromomethylimide was prepared from phthalhydroxymethylimide by the method of Pucher and Johnson (*J. Amer. Chem. Soc.*, 1922, **44**, 817), this being a great improvement on the older method of Sachs (*Ber.*, 1898, **31**, 1225). A solution of phthalbromomethylimide (100 g.) in dry xylene (500 c.c.) was boiled under reflux for 8 hours while a stream of dry ammonia gas was passed through it. The solid product which had separated was then filtered, crushed, and extracted with water and alcohol, and the insoluble residue was recrystallised from glacial acetic acid. *Triphthalimidotrimethyl-*